



Stereochemistry Study Guide

[Link to Series on jOeCHEM](#)

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Hi, gang, and welcome to the Stereochemistry study guide on jOeCHEM! If this is your **first** study guide (hey, welcome—glad you're here), let me provide some background for what I envision these guides to be and how they are supposed to help you kick organic butt.

For every series on jOeCHEM (aka "Gen Chem Boot Camp", for example), I want these study guides to be a central summary point. If you're starting to study for an exam, and you want to have a general idea of what is contained within a given unit, I hope you can turn to these study guides and get that overview.

Of course jOeCHEM can't be a perfect substitute for every Organic Chemistry class (each teacher/class is different), but I'll aim to include:

1. Terms you need to know + their definitions
2. An overview of all the key concepts in a given series
3. A summary of all the reactions specific to that series (this will be a thing when we start learning reactions)
4. Tips & Tricks I think could be helpful and may not necessarily fit in the other sections

Terms to Know

Below is a list of terms that you should have a working understanding of. There's a lot of science-y jargon in Organic Chemistry, so to be able to walk-the-walk (do reactions and stuff), we have to have to be able to talk-the-talk (talk and stuff).

- **Isomerism** – when a pair of molecules share a same ‘likeness’, such as: structural isomers, geometric isomers, or stereo isomers.
- **Structural Isomer** – a pair of molecules that have the same molecular formula but have different atom-to-atom connections. An example of this is butane & isobutane: they are both represented by C_4H_{10} but are laid out differently.
- **Geometric Isomer** – a pair of molecules that have the same molecular formula + atom-to-atom connections but are laid out differently in space due to a lack of rotation (i.e. due to double bond). For example, *trans*-2-butene and *cis*-2-butene are geometric isomers.
 - **cis** – when atoms or groups are on the same side of something, such as a double bond
 - **trans** – when atoms or groups are on the opposite side of something, such as a double bond
- **Stereochemical (Stereo) Isomer** – a pair of molecules that have the same molecular formula + atom-to-atom connections but at one or more carbons atoms are arranged in space differently.
- **Wedge** – a way to show a bond's 3D angle perspective on a 2D surface, off of an atom. On a piece of a paper, a wedge appears to come out of the paper, toward your face.
- **Dash** – a way to show a bond's 3D angle perspective on a 2D surface, off of an atom. On a piece of a paper, a dash appears to go through the paper, toward your feet.
- **Stereochemistry** – chemical properties caused by how groups of atoms are spatially arranged around individual atoms.
- **Chirality** – the property of a structure having a nonsuperimposable mirror image. For example, if you took your right hand, considered its mirror image (your left hand), and then tried to overlay your left hand on top of your right, you'd see that **it wouldn't match up**—this means your right hand is chiral.
 - Note: A structure will be chiral if BOTH of the following are true:
 - It has ≥ 1 or more stereocenters
 - There is NO internal plane of symmetry in the molecule
- **Achirality** – the opposite of chirality—a given structure's mirror image would be superimposable on it. For example, think of a cartoon heart: if you created a

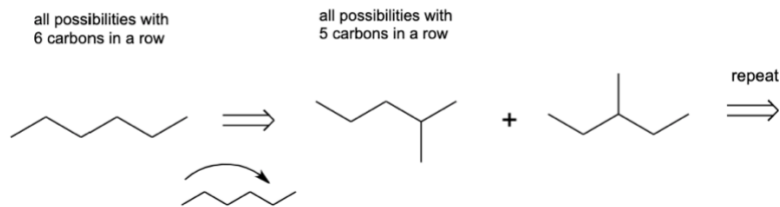
mirror of it and then tried to overlay it back on the original heart, it would line up perfectly. In that case, the heart would be achiral.

- **Chiral Center/Stereocenter/Stereogenic Center** – an atom that is attached to four different, unique groups (all four groups must have different molecular weights).
- **Plane Polarized Light** – a source of light that is passed through a filter of some kind, allowing light through that is only going in one direction.
- **Optical Activity** – when a sample of a structure (a solution of it) bends/rotates the plane of polarized light as the light passes through the solution. Chiral structures have a property where, when plane polarized light is passed through, light will be rotated clockwise or counterclockwise. Achiral structures will not rotate the plane of polarized light.
- **Dextrorotatory (+)** – when plane polarized light passes through a solution and is bent in a clockwise direction
- **Levorotatory (-)** – when plane polarized light passes through a solution and is bent in a counterclockwise direction
- **R/S configuration** – chiral centers can be labeled as having an ‘R’ or ‘S’ configuration. If the group priorities (‘1’ being applied to the heaviest group and ‘3’ to the lightest) go in a clockwise direction, it is ‘R’. If the priorities go counterclockwise, it is ‘S’.
 - Note: assigning ‘R’ and ‘S’ assumes that the lowest priority group (the lightest group by molecular weight, aka number ‘4’) is “facing away from you”. Looking at a piece of paper, this would appear as a dash.
- **Double Switch** – a trick to rotate bonds around a stereocenter and position the lowest priority group “away from you” to make assigning R & S easier. This involves taking a pair of groups, and switching their bond locations around a stereocenter. This inverts this stereochem, but doing an additional switch recovers the original stereochem and helps placing the lowest priority group away from you.
- **Internal Plane of Symmetry** – if a dotted line can be drawn through a structure and both sides on either side of the line match up with the other, the structure has an internal plane of symmetry.
- **Meso** – a structure that has an internal plane of symmetry. All meso structures are achiral since their mirror image will be superimposable.
- **Enantiomers** – a pair of structures (stereoisomers) that have identically opposite stereochem at each and every stereocenter.
 - For example, if a structure has three stereocenters, 1R, 3S, 6S, its enantiomer would have to have the following stereochemistry: 1S, 3R, 6R.
- **Diastereomers** – a pair of structures (stereoisomers) that DO NOT have identically opposite stereochem at each and every stereocenter, but the stereochemistry is different from one another.

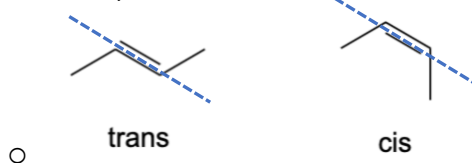
- For example, if a structure has three stereocenters, 1R, 3S, 6S, one diastereomer would have to have the following stereochemistry: 1R, 3R, 6R. Another one could be 1S, 3S, 6S.
 - Note: a given structure will only ever have one enantiomer but could have ≥ 1 diastereomer (depending on how many chiral center exist in the structure)
- **Fischer Projection** – a different way to visualize structures where they are drawn top to bottom. At each “intersection”:
 - Atoms on the left and right hand side are wedges and are “coming out at you” (think of two arms coming out of the page to hug you 😊).
 - Atoms on the top and bottom are dashes and are “away from you”

Overview of Concepts

- Structural Isomerism - a common problem is to “draw all the structural isomers for *insert alkane name*”, such as *hexane*. A good strategy for these types of problems is the following:



- 1.) Draw the original structure and take a carbon from an end, shortening the chain length by 1 (e.g. 6 → 5) and generate as many new structures as possible (without duplicates) using that plucked end carbon as a branch
 - 2.) Repeat step 1. with all the newly created structures. For example, with the hexane, take all the new 5 chain length structures, remove a carbon from an end, and create new 4 chain structures with new branch combos.
- Geometric Isomerism – if you go from one end of the structures shown below, you can either cross an imaginary dotted line or stay on the same side of the line: if you cross, the double bond is **trans**. If you don't cross, it is **cis**.



- Stereoisomerism – you will often be asked to identify if 2 structures are stereoisomers, and if so, what kind. To do this, do the following:
 - Verify that the structures have the same chemical formula (sometimes people will be sneaky and give you two different structures) and are chiral
 - Identify all stereocenters in the molecules and assign R & S
 - Compare all of the stereocenters. If they are opposite you have **enantiomers**. If they are different but not opposite, you have **diastereomers**.

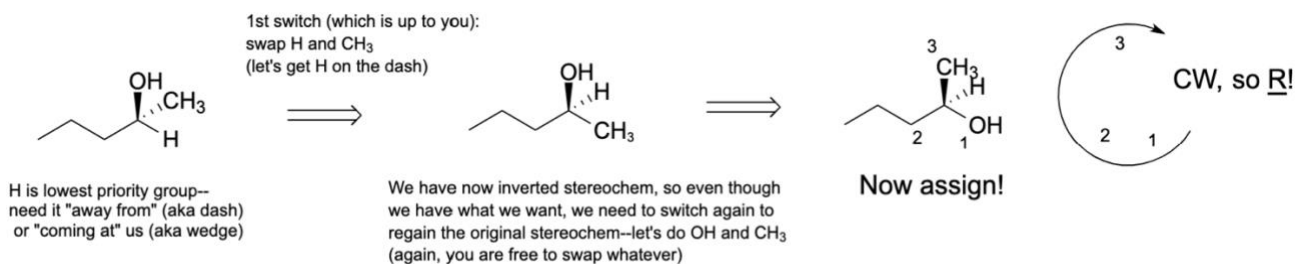


- Assigning R & S
 - 1.) Check that the stereocenter in question has 4 different groups (by molecularly/atomic weight) attached. If it doesn't, it's not a stereocenter 😊
 - *Remember to break ties by listing out what is additionally attached to the atoms that have tied.
 - 2.) Ensure the lightest atom/group aka the lowest priority group is positioned conveniently for you, either **away** from you or **coming at** you

*Per R & S assigning convention, the lowest priority group should be facing away from you, but if it's coming at you, you can assign and take the opposite result. If it's on a straight line, you can employ the Double Switch.

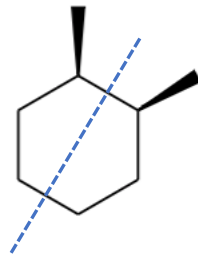
- 3.) Assign priorities 1-3 (excluding the lowest priority group), giving 1 to the heaviest group and 3 to the lightest.
- 4.) Draw a line CW or CCW, starting at 1 and going around to 3: if the line is going CW the configuration is R but if CCW it is S.
- The Double Switch – If your lowest priority group is on a straight line (aka in the plane of the page), you have two choices:
 - Do mental gymnastics and visualize the perspective where that group is “away” from you (it hurts the brain, in my opinion)
 - Perform a double switch, where you swap 2 pairs of groups around your stereocenter **two** times and end up placing the lowest priority group “away”. Each group swap around a stereocenter inverts the stereochem, so since we only have 2 options for configurations (R & S), doing one swap inverts the stereochem, but doing a 2nd swap recovers the original stereochem:

Below is a double swap example:



- Chirality & Optical Activity
 - If something is chiral, it is optically active aka it rotates the plane of polarized light as the light passes through that given substance/solution.
 - If something is achiral, it is optically inactive and DOES NOT rotate the plane of polarized light.
 - Something will be chiral IF:
 - It has ≥ 1 or more stereocenters
 - There is NO internal plane of symmetry in the molecule (aka it is NOT meso)
- Meso + Internal Plane of Symmetry
 - If you can draw a dotted line through a structure and it is symmetrical on both sides, that means the structure has an internal plane of symmetry and is **meso**.
 - As a result, due to the plane of symmetry, the structure's mirror image will be superimposable—meso structures are ALWAYS achiral aka optically inactive.

An example of a meso structure (which is achiral, despite having 2 stereocenters!) is shown below:



Summary of Reactions

Luckily, there are no reactions for this section

Tips, Tricks & General Advice

- Be very comfortable with:
 - *Assigning R & S. You'll need to do it quickly and most likely under pressure. If it's muscle memory, you'll save lots of time on tests/exams
 - *Understanding what chirality is and how to identify when something is/isn't. Very often, someone will ask you if something is "optically active", and that is them asking you whether someone is chiral or not
 - The different types of isomerism.
- Know your definitions and terms. This section is insane with how much new terminology there is: if you aren't clear on something PLEASE ask someone. This is not the time to hope something will go away if you aren't clear on it (stereochem sticks around for the long haul).
- Remember Fischer Projection conventions. Some courses don't introduce them this early, but some do & that's why I've included them in this section.