



# Alkanes Study Guide

[Link to Series on jOeCHEM](#)

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Hi, gang, and welcome to the Alkanes 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).

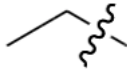

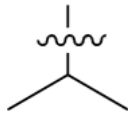
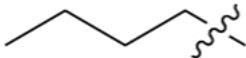
- **Functional Group** – a group of one or more atoms within a molecule that has certain chemical behaviors, usually allowing for chemical reactions to take place
- **Boiling Point** – the temperature at which a molecule begins transitioning from the liquid to the gaseous phase
- **Melting Point** – the temperature at which a molecule begins transitioning from the solid to the liquid phase
- **Common Naming** – a manner in which to name organic molecules if they've been given a "common" name. Not all molecules have one, but typically smaller compounds will (e.g. tert-butyl bromide versus 2-bromo-2-methylpropane)
- **IUPAC Systematic Naming** – a more formal naming system which can be used to name **any** organic molecule, whether it has a common name or not
- **Parent Chain** – the longest/most prominent chain of consecutive carbons in a molecule you're naming
- **Substituents (in the context of naming)** – a group of off the Parent Chain currently under consideration
- **Functional Group Priority** – when naming molecules with more than one type of functional group, always defer to the "highest" priority group. These priorities have been defined by the IUPAC folks, and you can find a list [here](#) (but defer to your course's list if it differs from mine)
- **Newman Projection** – a visual way to represent a structure, looking down a single bond axis of 2 carbons, in order to see how the internal energy of that changes. The energy changes because single bonds off of the carbons are constantly rotating and sometimes bigger or smaller groups get closer to each other
- **Staggered Conformation** – any conformation of a Newman Projection when the bonds on the front and back carbons are NOT aligned—there is "daylight" between the front and back bonds
- **Eclipsed Conformation** – any conformation of a Newman Projection when the bonds on the front and back carbons ARE aligned—there is NO "daylight" between the front and back bonds
- **Anti (in Newman Projection context)** – the specific conformation of a Newman Projection for a molecule when the two largest groups on the front carbon and back carbon are 180° opposite from each other. This is always a staggered conformation

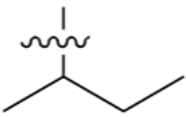
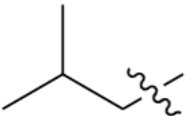


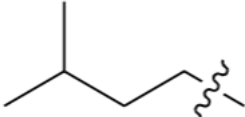

- **Gauche** – the specific conformation of a Newman Projection for a molecule when the two largest groups on the front carbon and back carbon are  $60^\circ$  opposite from each other. This is always a staggered conformation
- **Steric Strain** – strain between groups caused by being in close proximity & “bumping” one another. The bigger two groups are and the closer they are, the more steric strain exists
- **Torsional Strain** – strain caused by two groups’ electrons repelling one another. The closer two groups are, the greater this electrostatic repulsion is which means more torsional strain
- **Ring Strain** – strain caused by a cyclic structure not allowing the atoms within the ring to assume the bond angles they would prefer. For example, in cyclobutane, the  $sp^3$  carbons want to have  $109.5^\circ$  bond angles, but the best shape that can be achieved is a square and  $\sim 90^\circ$  angles—that difference in angle causes strain
- **Cyclohexane Chair Conformation** – the special 3D conformation cyclohexane assumes to achieve  $109.5^\circ$  bond angles (which makes it the best in the game). Every chair can “flip” to its other form
- **Chair Flip** – when a cyclohexane chair flips to its other chair form. This happens all the time, and sometimes one chair form can be more energetically favor than its counterpart
- **Equatorial** – a substituent on a cyclohexane ring that is either **slightly** up or down
- **Axial** – a substituent on a cyclohexane ring that is either **straight** up or down
- **Cyclohexane “Peak”** – a peak on a cyclohexane chair is a position that is higher than its neighbors, and positions are axial up and equatorial down
- **Cyclohexane “Valley”** – a valley on a cyclohexane chair is a position that is lower than its neighbors, and positions are axial down and equatorial up
- **Cyclohexane Boat Conformation** – when a cyclohexane chair flips from one chair form to another, a **boat** conformation is passed through. This conformation is **unstable** and only exists for a brief instant. It is so unfavorable because of **transangular strain**
- **Transangular Strain** – strain experienced in cyclic structures where groups on opposite ends of the ring repel/bump into one another. This occurs in cyclohexane boat conformations
- **Radical** – any atom that has a single, unpaired electron. Radical atoms are  $sp^2$  hybridized & therefore have a trigonal planar geometry. The radical electron is housed in an unhybridized p orbital
- **Hyperconjugation** – the stabilizing effect where a carbon’s radical electron (house in a **p** orbital) mimics a pi bond (momentarily) with the bonds of neighboring carbons

- **Free Radical Halogenation** – very likely the first reaction you'll learn (yay!). Allows us to create alkyl halides from bland, plain alkanes (aka put a Cl or Br on an alkane)
- **Chain Reaction** – a reaction that produces the very thing it needed to get started (e.g. Free Radical Halogenation producing a radical Cl or Br in the propagation 2 step)
- **Hammond's Postulate** – a concept that states that:
  - exothermic, fast reactions/reaction steps occur quickly such that if you examine the transition state it will look more like the **reactants** versus the products. This is referred to as an "early transition state"
  - endothermic, slow reactions/reaction steps occur slowly and therefore have transition states that resemble the **products** versus the reactants. This is referred to as a "late transition state"

# Overview of Concepts

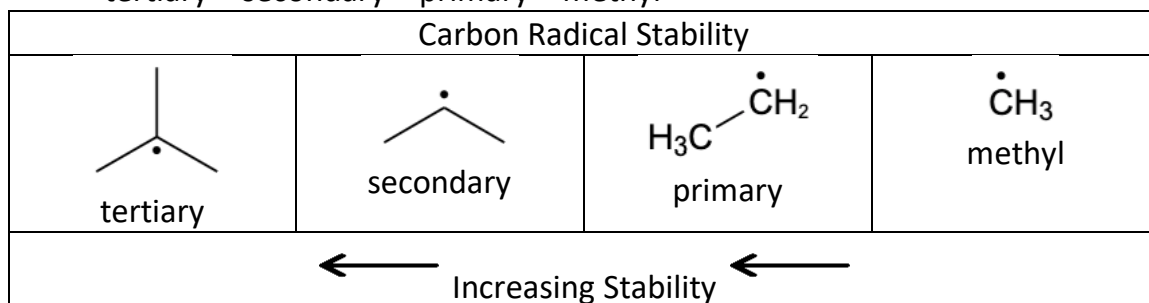
- Functional Groups
  - Memorize. All. Of. Them. If you aren't asked about them explicitly, not knowing them off the top of your head will haunt you throughout OChem I and II.
  - Consult the list provided by your instructor or do a quick Google search for "organic chemistry functional groups"
- Boiling Point
  - the heavier (aka more carbons/heavy atoms) a structure is, the higher the boiling point. If you have a tie with molecular weight, go with the structure that is **less** branched
- Melting Point
  - the heavier (aka more carbons/heavy atoms) a structure is, the higher the melting point. If you have a tie with molecular weight, go with the structure that is **MORE** branched (opposite of boiling point)
- Common Naming:

# of Carbons	Appearance/ Attachment Point	Prefix
1	CH <sub>3</sub> -	methyl _____
2		ethyl _____
3		propyl _____
3		isopropyl _____
4		butyl _____

4		sec-butyl ____
4		isobutyl ____
4		tert-butyl ____
5		pentyl ____
5		isopentyl ____
5		neopentyl ____

- IUPAC Systematic Naming
  - Visit the [IUPAC Naming worksheet](#) (and [solution](#)) for the process outlined and to practice practice, practice
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- IUPAC Systematic Naming with Functional Groups
  - Visit the [IUPAC Naming worksheet](#) (and [solution](#))

- Have handy a [functional group priority list](#) (or ideally one given to you by your instructor)
- Newman Projections
  - Knowing that single bonds are constantly, always rotating, Newman Projections give us a way to illustrate how, at different points in time, various bonds get closer to other ones and raise/lower the energy of a molecule
  - In terms of drawing Newman Projections:
    1. Identify the two carbons you want to draw a Newman Projection for, and designate one to be the “front” carbon and the other as the “back” carbon
    2. Draw the initial Newman Projection
    3. Produce all of the other Newman Projection conformations, taking the initial conformation and rotation **only** the front groups OR the back groups, but NOT both at the same time
      - a. Rotate 60° at a time, going from staggered to eclipsed OR eclipsed to staggered on each rotation
    4. If you have to pick out a low/high energy conformation look at the structures and consider which ones have the most/least energy based on the strain present
      - a. The “anti” conformation will be your lowest E structure (it is staggered and has the two largest groups farthest away from each other)
- Cyclohexane chairs
  - Be comfortable taking a bond-line cyclohexane derivative (a cyclohexane with substituents) and drawing the 2 corresponding cyclohexane chairs
  - When comparing 2 chair conformations of a structure, be able to identify the lowest energy chair conformation
- Free Radical Halogenation
  - Carbon radical stability INCREASES as a carbon is more substituted:  
tertiary > secondary > primary > methyl



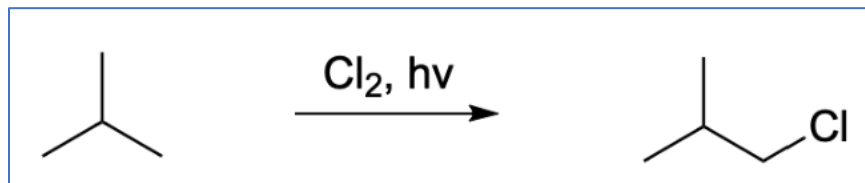
- This reaction is a **chain reaction**: by the reaction occurring itself, more radical halogen is created to continue reacting
- Chlorine is a more exothermic reaction and is thus **less selective** in terms of where it will end up on a structure. It will gravitate to being attached to the most “abundant” position aka a carbon position that has the most hydrogens
- Bromine is a less exothermic reaction (almost endothermic) and is thus **MORE selective** in terms of where it will end up on a structure. It will gravitate to being attached to the most substituted carbon
- Hammond’s Postulate
  - A very exothermic reaction will have an **early** transition state, and the transition state will look more like reactants as opposed to products
  - An endothermic reaction will have a **late** transition state, and the transition state will look more like products as opposed to reactants



# Summary of Reactions

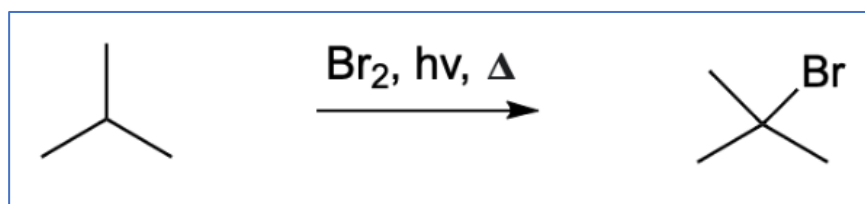
Below is a list of reactions related to this series that you should have a working understanding of. There's a lot of science-y jargon in Organic Chemistry, so to be able to walk-the-walk (do reactions and stuff), we have to have to be able to talk-the-talk (talk and stuff).

## Free Radical Chlorination



- Reaction Characteristics/Things to note:
  - A chloride is placed on an alkane by breaking a C-H bond
  - Chlorination is less "selective" than bromine due to the overall reaction's exothermic nature, so your "major" product will be the position with the most H's in the molecule

## Free Radical Bromination



- Reaction Characteristics/Things to note:
  - A bromide is placed on an alkane by breaking a C-H bond
  - Bromination is VERY "selective": Your "major" product will be the most substituted carbon in the molecule

# Tips, Tricks & General Advice

- Bear down and memorize the things you need to memorize. I hate brute force memorization, but for the following, you'll need to commit it to memory to be successful in organic chemistry:
  - Functional Groups (this will end up being free points on a test or quiz at some point—don't miss them)
  - Common naming (be automatic at this)
  - Names of carbon chains  $\leq 20$  (methane, ethane...decane, undecane...). If your teacher tells you a more specific # of carbons to memorize up until to, do that; otherwise, going up to 20 is generally pretty safe
- Put in the time to be able to confidently name structures in an IUPAC systematic fashion
- Be comfortable with all the Newman Projection vocabulary (anti, gauche, staggered, eclipsed, etc), generating all the conformations for a given structure, and ranking the relative energies of all those conformations
- Be comfortable working with cyclohexane chairs and ranking conformations in terms of their energies. Feel confident knowing whether to place groups axial up/down or equatorial up/down
- Know the free radical halogenation reaction well, both the mechanism and how to predict a reaction product