

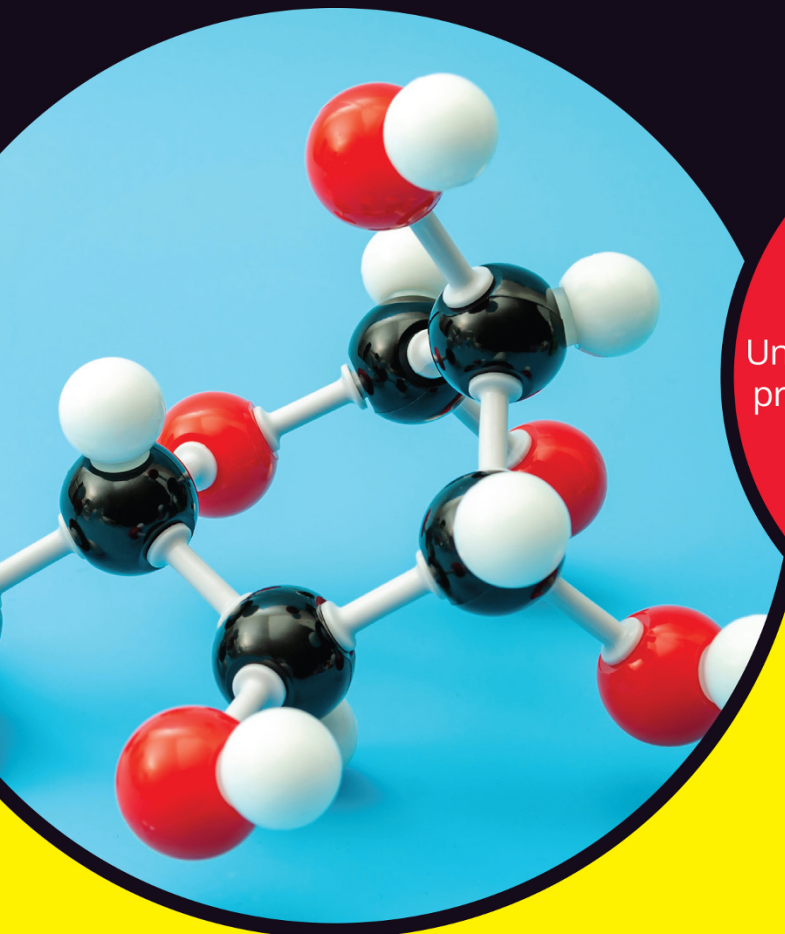
LEARNING MADE EASY



2nd Edition

Organic Chemistry II

for
dummies[®]
A Wiley Brand



Grasp
organic reactions

Understand physical and chemical
properties of organic compounds

Observe from macroscopic
and microscopic views

John T. Moore, EdD
Richard H. Langley, PhD
Professors of Chemistry



Organic Chemistry II

2nd Edition

by John T. Moore, EdD, and
Richard H. Langley, PhD

for
dummies[®]
A Wiley Brand

Organic Chemistry II For Dummies®, 2nd Edition

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Introduction

Welcome to *Organic Chemistry II For Dummies*. We're certainly happy you decided to delve further into the fascinating world of organic chemistry. It's a complex area of chemistry, but understanding organic chemistry isn't really that difficult. It simply takes hard work, attention to detail, some imagination, and the desire to know. Organic chemistry, like any area of chemistry, isn't a spectator sport. You need to interact with the material, try different study techniques, and ask yourself why things happen the way they do.

Organic Chemistry II is a more intricate course than the typical freshman introductory chemistry course, and you may find that it's also more involved than Organic I. You may actually need to use those things you learned (and those study habits that you developed) in Organic I to be successful in Organic II. But if you work hard, you can get through your Organic II course. More importantly, you may grow to appreciate the myriad chemical reactions that take place in the diverse world of organic chemistry.

About This Book

Organic Chemistry II For Dummies is an overview of the content covered in the second half of a typical college-level organic chemistry course. We've made every attempt to keep the material as current as possible, but the field of chemistry is changing ever so quickly — new reactions are always being developed. The basics, however, stay the same, and that's where we concentrate our attention.

While you flip through this book, you see many chemical structures and reactions. Much of organic chemistry involves knowing the structures of the molecules involved in organic reactions. If you're in an Organic Chemistry II course, you made it through the first semester of organic chemistry, so you probably recognize many of the structures, or at least the functional groups, from your previous semester's study.



TIP

If you bought this book just to gain general knowledge about a fascinating subject, try not to get bogged down in the details. Skim the chapters. If you find a topic that interests you, stop and dive in. Have fun learning something new.

If you're taking an organic chemistry course, you can use this rather inexpensive book to supplement that very expensive organic chemistry textbook. Then, when you complete your course, you can put it on your bookshelf as a conversation piece, alongside *Chemistry For Dummies*, by your intrepid author, John Moore (Wiley), *The Doctor Who Error Finder*, by R.H. Langley (McFarland), and *A Brief History of Time*, by Stephen Hawking (Bantam Dell). Or you can look forward to adding a copy of *Biochemistry For Dummies*, also by the authors of this book (Wiley), beside it.

Conventions Used in This Book

We've organized this book in a logical progression of topics; your second semester organic chemistry course may progress similarly. In addition, we set up the following conventions to make navigating this book easier:

- » *Italics* introduce new terms that you need to know.
- » **Bold** text highlights keywords within a bulleted list.
- » We make extensive use of illustrations of structures and reactions. While you read, try to follow along with the associated figures, whether they be structures or reactions.

Foolish Assumptions

We assume — and we all know about the perils of assumptions — that you're one of the following:

- » A student taking a college-level organic chemistry course.
- » A student reviewing organic chemistry for some type of standardized exam (the MCAT, for example).
- » An individual who just wants to know something about organic chemistry.

If you fall into a different category, you're special — and we hope you enjoy this book, too.

Icons Used in This Book

If you have ever read other *For Dummies* books (such as the wonderful *Chemistry For Dummies* or *Biochemistry For Dummies*, written by the two authors of this book and published by Wiley), you recognize the icons we use. The following five icons can guide you to certain kinds of information:



REMEMBER

This icon is a flag for those really important things that you shouldn't forget while you go deeper into the world of organic chemistry.



REAL
WORLD

The Real World icon points out information that has a direct application in the everyday world. These paragraphs may also help you understand the bigger picture of how and why organic mechanisms are in place.



TIP

We use this icon to alert you to a tip on the easiest or quickest way to learn a concept. Between the two of us, we have over 70 years of teaching experience. We picked up a few tricks along the way, and we don't mind sharing.



WARNING

The warning icon points to a procedure or potential outcome that can be dangerous. We call it our Don't-Try-This-At-Home icon.



TECHNICAL
STUFF

We try to avoid getting too technical throughout this book (believe it or not), but every now and then, we can't help but throw something in that's a little more in-depth than you might need. You can't hurt your education by just skipping it.

Beyond the Book

In addition to the material in this printed book, go to www.dummies.com to find a Cheat Sheet with study tips and exam-taking advice. To access this resource, simply type "Organic Chemistry II For Dummies Cheat Sheet" in the search box on Dummies.com.

Where to Go from Here

The answer to this question really depends on your prior knowledge and goals. Like with all *For Dummies* books, this one attempts to make all the chapters independent so that you can dive right into the material that's causing you trouble without having to read other chapters first. If you feel comfortable with the topics covered in Organic Chemistry I, feel free to skip Part I of this book. If you want a general overview of organic chemistry, skim the book. And when you find a topic that interests you or one in which you really need help, take a deeper plunge into the chapter that deals with that topic.

And for all of you, no matter who you are or why you're reading this book, we hope you have fun reading it and that it helps you to understand and appreciate organic chemistry.

1

**Brushing Up
on Important
Organic
Chemistry I
Concepts**

IN THIS PART . . .

Refresh yourself on the basics from Organic Chemistry I.

Get up to speed on mechanisms and how to push electrons around with those curved arrows.

Review the structure, nomenclature, synthesis, and reactions of alcohols and ethers.

Tackle conjugated unsaturated systems.

Get the how-to on spectroscopic techniques, from the IR fingerprints to NMR shifts.

- » Reviewing the material you learned in Organic I
- » Previewing what you find out in Organic II

Chapter **1**

Organic Chemistry II: Here We Go Again!

If you're looking at this chapter, it's probably because you're getting ready to take the second half of organic chemistry, are in the midst of Organic II, or you're trying to figure out what Organic II covers in time to change your major from pre-med to art history. In any respect, you probably successfully completed Organic Chemistry I. Many of the study techniques (and coping mechanisms) you learned that helped you do well in Organic I are helpful in Organic II. The two primary things to remember are

- » *Never* get behind.
- » Carbon has four bonds.

In this book we use larger, more complex molecules than you may have encountered in Organic I. We chose to do this because, firstly, that's the nature of Organic II — larger and more complex molecules. Secondly, many of you will be taking biochemistry at some point, and to succeed in that subject you need to become comfortable with large, involved molecules. (If you do take biochemistry, be sure to check out *Biochemistry For Dummies* by John T. Moore and Richard H. Langley [Wiley]. We understand the authors are really great guys.)

To get you started, this chapter does a quick review of the topics commonly found in Organic I, and then gives an overview of what we cover in Organic II.

While you read over what you specifically need from Organic I, make sure you note anything you feel weak about so that you can do a quick review now.

Recapping Organic Chemistry I

In Organic I you learned that organic chemistry is the study of carbon compounds. Until the mid-1800s, people believed that all carbon compounds were the result of biological processes requiring a living organism. This was called the *vital force theory*. The synthesis (or formation) of urea from inorganic materials showed that other paths to the production of carbon compounds are possible. Many millions of organic compounds exist because carbon atoms form stable bonds to other carbon atoms. The process of one type of atom bonding to identical atoms is *catenation*. Many elements can catenate, but carbon is the most effective, with apparently no limit to how many carbon atoms can link together. These linkages may be in chains, branched chains, or rings, providing a vast number of compounds.

Carbon is also capable of forming stable bonds to a number of other elements, including the biochemically important elements hydrogen, nitrogen, oxygen, and sulfur. The latter three elements form the foundation of many of the functional groups you studied in Organic I, while hydrogen is in nearly every organic compound.

Intermolecular forces

You learned about intermolecular forces in Organic I. Intermolecular forces (forces between chemical species) are extremely important in explaining the interaction between molecules. Intermolecular forces that you saw in Organic I and see again in Organic II include dipole-dipole interactions, London, hydrogen bonding, and sometimes ionic interactions.

Dipole-dipole forces exist between polar regions of different molecules. The presence of a dipole means that the molecule has a partially positive ($\delta+$) end and a partially negative ($\delta-$) end. Opposite partial charges attract each other, whereas like partial charges repel.

Hydrogen bonding, as the name implies, involves hydrogen. This hydrogen atom must be bonded to either an oxygen atom or a nitrogen atom. (In nonbiological situations, hydrogen bonding also occurs when a hydrogen atom bonds to a

fluorine atom.) Hydrogen bonding is significantly stronger than a normal dipole-dipole force, and is much stronger than London dispersion forces, the forces between nonpolar molecules due to the fluctuations of the electron clouds of atoms or molecules. The hydrogen bonded to either a nitrogen or oxygen atom is strongly attracted to a different nitrogen or oxygen atom. Hydrogen bonding may be either intramolecular or intermolecular.

In organic reactions, ionic interactions may serve as intermolecular or intramolecular forces. In some cases, these may involve metal cations, such as Na^+ , or anions, such as Cl^- . Cations may include an ammonium ion from an amino group, such as RNH_3^+ . The anion may be a carboxylate ion, such as RCOO^- from a carboxylic acid. The oppositely charged ions attract each other very strongly (stronger than the other intermolecular interactions).

Functional groups

Carbon is an extremely versatile element because it can form many different compounds. Most of the compounds you see have one or more *functional groups*, which contain atoms other than carbon and hydrogen and/or double or triple bonds, and define the reactivity of the organic molecule.

In Organic I you probably started with the hydrocarbons, compounds of carbon and hydrogen, including the alkenes and alkynes that contained double and single bonds, respectively. Then you probably touched on some of the more common functional groups, such as alcohols and maybe even some aromatic compounds.

Reactions

You encountered many reactions in Organic I. Every time you encountered a different functional group, you had a slew of reactions to learn. Reactions that told how the functional group could be formed, common reactions that the functional group underwent — reactions, reactions, and more reactions.

Two of the most important ones you learned were substitution and elimination reactions: $\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$, E1, and E2. We hope you learned them well because you'll be seeing them again quite often.

Spectroscopy

In Organic I you probably covered different types of spectroscopy and how they're used in structure determinations. You discovered how mass spectroscopy can give you an idea about molar mass and what fragments may be present in the molecule. You found out that infrared spectroscopy can be used to identify functional

groups, and you learned to look at the fingerprint region. Then finally you progressed to nuclear magnetic resonance (NMR) spectroscopy, one of the main tools of organic chemists, which can be used to interpret chemical shifts and splitting patterns to give you more clues about structure.

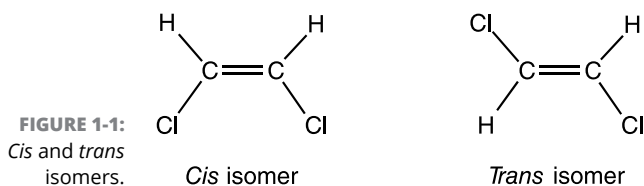
Isomerism and optical activity

During Organic I you were exposed to the concepts associated with isomerism and optical activity. You need to be familiar with these concepts in Organic II, so we take a few minutes here for a brief review.

Isomers are compounds that have the same molecular formula but different structural formulas. Some organic and biochemical compounds may exist in different isomeric forms, and these different isomers have different properties. Two common types of isomers in organic systems are *cis-trans* isomers and isomerism due to the presence of a chiral carbon.

Cis-trans isomers

The presence of carbon-carbon double bonds leads to the possibility of isomers. Double bonds are rather restrictive and limit molecular movement. Groups on the same side of the double bond tend to remain in that position (*cis*), while groups on opposite sides tend to remain across the bond from each other (*trans*). You can see an example of each in Figure 1-1. However, if the two groups attached to either of the carbon atoms of the double bond are the same, *cis-trans* isomers are not possible. *Cis* isomers are the normal form of fatty acids, but processing tends to convert some of the *cis* isomers to the *trans* isomers.



Cis-trans isomers are also possible in nonaromatic cyclic systems. The *cis* form has similar groups on the same side of the ring, while the *trans* form has similar groups above and below the ring.

Chiral compounds

A carbon atom that has four different groups attached is *chiral*. A chiral carbon rotates plane-polarized light, light whose waves are all in the same plane, and has

an *enantiomer* (non-superimposable mirror image). Rotation, which may be either to the right (dextrorotatory) or to the left (levorotatory), leads to one optical isomer being *d* and the other being *l*. Specific rotation (represented by $[\alpha]_D^T$, where α = observed rotation, T = temperature, and D = sodium D line) is a measure of the ability of a compound to rotate light. The specific rotation comes from the observed rotation (α) divided by the product of the concentration of the solution and the length of the container. Other than optical activity, the physical properties of enantiomers are the same.

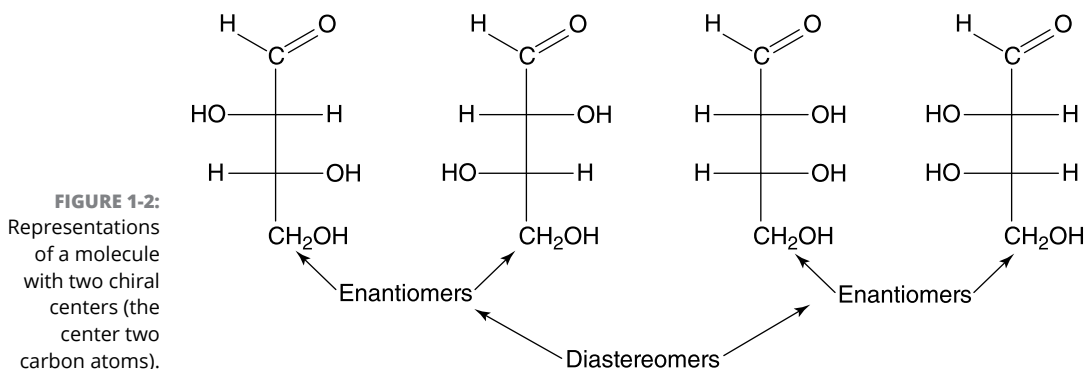
A *racemic mixture* is a 50:50 mixture of the enantiomers.

A *meso compound* is a compound with chiral centers and a plane of symmetry. The plane of symmetry leads to the optical rotation of one chiral carbon cancelling the optical rotation of another.

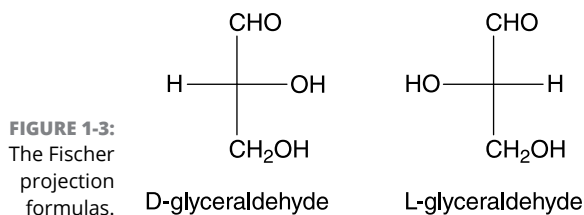
Diastereomers are stereoisomers that aren't enantiomers.

R-S notation is a means of designating the geometry around the chiral center. This method requires the groups attached to the chiral center to be prioritized in order of decreasing atomic weight. To assign the center, place the lowest priority group (the group that has the lowest atomic weight) on the far side and count the remaining groups as 1, 2, and 3. Counting to the right is *R* and counting to the left is *S*. Any similarity between *d* and *l* and *R* and *S* is coincidental.

Some important organic compounds have more than one chiral center. Multiple chiral centers indicate the presence of multiple stereoisomers. The maximum number of stereoisomers is 2^n where n is the number of nonidentical chiral centers. Figure 1-2 shows the four stereoisomers present in a molecule that has two chiral centers. Non-superimposable mirror images are enantiomers, while the other species in the figure are diastereomers. Unlike enantiomers, diastereomers have different physical properties.



Emil Fischer developed a method of drawing a compound to illustrate which stereoisomer is present. Drawings of this type, called *Fischer projection formulas*, are very useful in biochemistry. In a projection formula, a chiral carbon is placed in the center of a + pattern. The vertical lines (bonds) point away from the viewer, and the horizontal lines point towards the viewer. Fischer used the *D* designation if the most important group was to the right of the carbon, and the *L* designation if the most important group was to the left of the carbon. (See Figure 1-3.)



The use of *D* and *L* is gradually being replaced by the *R* and *S* system of designating isomers, which is particularly useful when more than one chiral carbon atom is present.

Looking Ahead to Organic Chemistry II

One of the keys to Organic II is *mechanisms*, the specific way in which a reaction proceeds. Recall from Organic I that this involves pushing around electrons, showing where they're going with curved arrows. We give you a good review of these concepts in Chapter 2, along with some basic reaction moves.

In Chapter 3 we go into some depth about alcohols and ethers. Like Organic I, when we encounter a new functional group we examine the structure, nomenclature, properties, synthesis, and reactions. In some courses and textbooks, alcohols are covered in the first semester, but for those readers who haven't gotten to them yet, we include them in this book. If you're already comfortable with that material, please feel free to skip that chapter and go on to another.

Conjugated unsaturated systems are an important part of organic chemistry, so in Chapter 4 we spend a little time talking about those systems, setting the stage for our discussion of aromatic compounds that you can find in Chapter 6.

To bring you up to speed on spectroscopy, we cover the basics in Chapter 5. We give you the executive summary on infrared (IR), ultraviolet-visible (UV-vis), mass spectrometry (mass spec), and nuclear magnetic resonance (NMR). In addition, many of the chapters in this book have a spectroscopy section at the end where we cover the essentials concerning the specific compounds that you study in that chapter.

Aromatic compounds and their reactions are a big part of any Organic II course. We introduce you to the aromatic family, including the heterocyclic branch, in Chapter 6. (You may want to brush up on the concept of resonance beforehand.) Then in Chapters 7 and 8, you find out more than you ever wanted to know about aromatic substitution reactions, starring electrophiles and nucleophiles.

Another important part of Organic II is carbonyl chemistry. We look at the basics of the carbonyls in Chapter 9. It's like a family reunion where I (John, one of your authors) grew up in North Carolina — everybody is related. You meet aldehydes, ketones, carboxylic acids, acyl chlorides, esters, amides, and on and on. It's a quick peek, because later we go back and examine many of these in detail. For example, in Chapter 10 you study aldehydes and ketones, along with some of the amines, while in Chapter 11 we introduce you to other carbonyl compounds, enols and enolates, along with nitroalkanes and nitriles.

Carboxylic acids and their derivatives are also an important part of Organic II. We spend quite a few pages looking at the structure, nomenclature, synthesis, reactions, and spectroscopy of carboxylic acids. While on this topic in Chapter 12, we use a good deal of acid-base chemistry, most of which you were exposed to in your introductory chemistry course. (For a quick review, look over a copy of *Chemistry For Dummies* or *Chemistry Essentials For Dummies*, both written by John T. Moore and published by Wiley.)

Carbon compounds that also contain nitrogen, such as the amines, play a significant part of any Organic II course. You encounter more acid-base chemistry with the amines, along with some more reactions. We hit this topic in Chapter 13 and give you some tips for multistep synthesis.

You probably haven't considered the fact that some organic compounds may contain a metal, so we give you an opportunity to become familiar with the organometallics in Chapter 14. In this chapter you meet the Grignard reaction. It's a very important organic reaction that you may have the opportunity to run in organic lab.

You just can't get away from those carbonyls, so you get another taste of these reactions, many of them named reactions, in Chapter 15. You may be able to avoid biomolecules if your course doesn't cover them, but if it does, Chapter 16 is there for you.

Finally, what's a good organic course without multistep and retrosynthesis along with roadmaps? We hope that our tips can ease your pain at this point. Roadmaps are the bane of most organic chemistry students, but just hang in there. There is life after organic chemistry, and you may just find in the end that you actually enjoyed organic. And for those of you who missed the chemical calculations, there's always quantitative analysis and physical chemistry.

- » Analyzing arrows
- » Breaking down basic moves
- » Contemplating combining basic moves
- » Mastering free-radical mechanisms

Chapter 2

Remembering How We Do It: Mechanisms

Mechanisms are the key to organic chemistry. Understanding the mechanism allows organic chemists to control the reaction and to avoid unwanted side reactions. Many times, understanding the mechanism allows chemists to increase the yield of product.

In this chapter you review the basics of mechanisms and their conventions and look at some of the more common ways that electrons shift during a reaction. You also see how these individual steps can fit together in the overall reaction mechanism and apply some of these techniques in free-radical mechanisms.

Duck — Here Come the Arrows

Many types of arrows are used in organic chemistry, and each of them conveys information about the particular reaction. These arrows include the resonance arrow, equilibrium arrow, reaction arrow, full-headed curved arrow, and half-headed curved arrow.

The *resonance arrow*, a single line that has arrow heads at both ends (see Figure 2-1), separates different resonance structures. The actual structure is a weighted average of all resonance forms. More resonance forms usually indicate a more stable structure. One or more of the resonance structures may be useful in predicting what will happen during a reaction (a mechanism).

FIGURE 2-1:
The resonance
arrow.



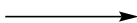
The *equilibrium arrow*, which has two lines pointing in opposite directions (see Figure 2-2), separates materials that are in equilibrium. Materials on each side of the arrow are present. Unlike a resonance arrow, the materials actually exist and aren't a hybrid. If one of the arrows is longer than the other, it indicates that one side of the equilibrium predominates over the other.

FIGURE 2-2:
The equilibrium
arrows.



A *reaction arrow*, a single arrow pointing in one direction (see Figure 2-3), simply separates the reactants from the products. The use of this arrow usually indicates that the reaction proceeds in only one direction (unlike the equilibrium arrow).

FIGURE 2-3:
The reaction
arrow.



Full- and half-headed curved arrows indicate the movement of electrons. *Full-headed curved arrows* (shown in Figure 2-4a) show the movement of two electrons, whereas *half-headed curved arrows* (Figure 2-4b) indicate the movement of one electron. The electrons always move in the direction indicated by the arrow. The head (point) of the arrow is where the electron is going, and the tail is the electron's source.

FIGURE 2-4:
Curved arrows
indicating the
movement of
electrons.

