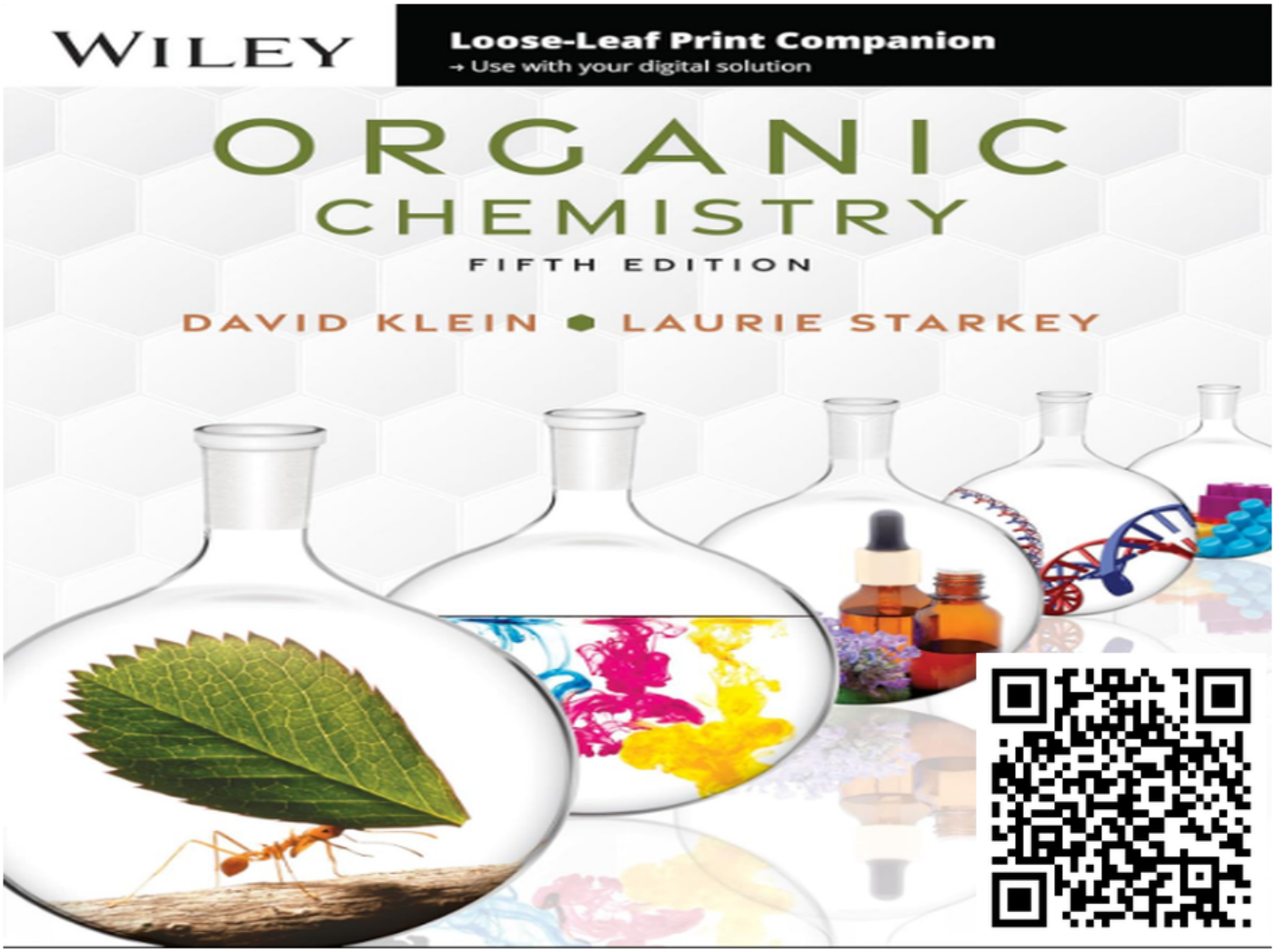

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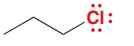
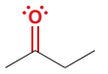
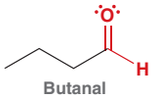
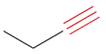
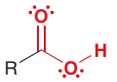
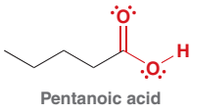
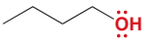
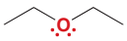
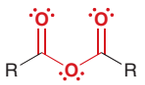
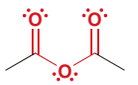
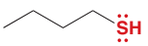
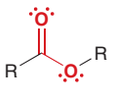
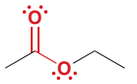
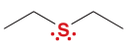
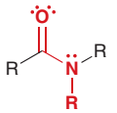
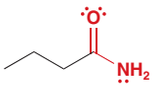
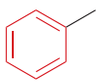
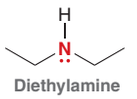
ORGANIC CHEMISTRY

FIFTH EDITION

DAVID KLEIN ● LAURIE STARKEY

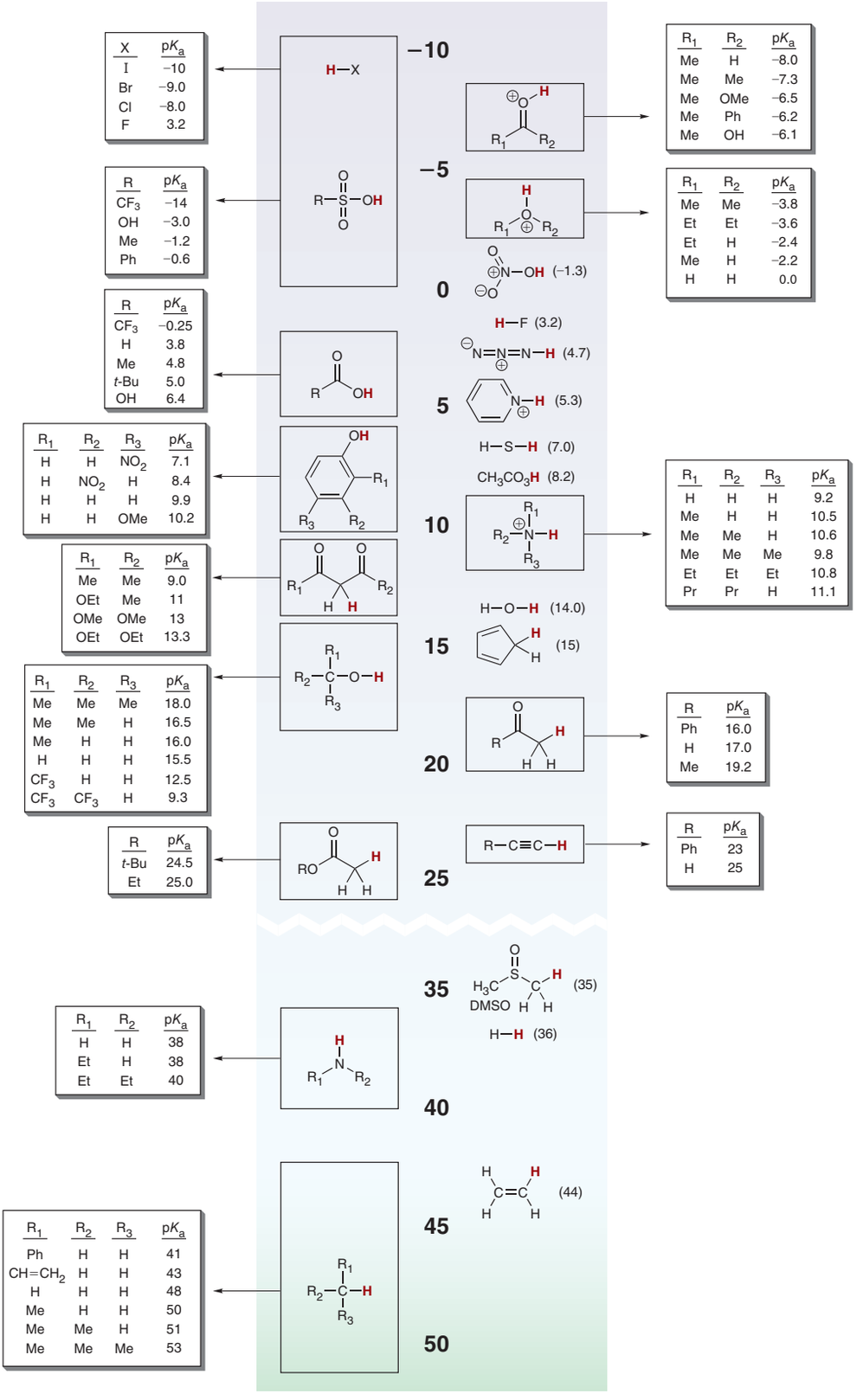
ISBN 978-1-394-18937-3
90000
9 781394 189373

EXAMPLES OF COMMON FUNCTIONAL GROUPS

FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER	FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER
R—X: (X = Cl, Br or I)	Alkyl halide	 *n*-Propyl chloride	7		Ketone	 2-Butanone	19
	Alkene	 1-Butene	7, 8		Aldehyde	 Butanal	19
R—C≡C—R	Alkyne	 1-Butyne	9		Carboxylic acid	 Pentanoic acid	20
R—OH	Alcohol	 1-Butanol	12		Acyl halide	 Acetyl chloride	20
R—O—R	Ether	 Diethyl ether	13		Anhydride	 Acetic anhydride	20
R—SH	Thiol	 1-Butanethiol	13		Ester	 Ethyl acetate	20
R—S—R	Sulfide	 Diethyl sulfide	13		Amide	 Butanamide	20
	Aromatic (or arene)	 Methylbenzene	17, 18		Amine	 Diethylamine	22

* The "R" refers to the remainder of the compound, usually carbon and hydrogen atoms.

Approximate pK_a Values for Commonly Encountered Structural Types



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Dedication

To my father and mother (may you both rest in peace),

You have saved me (quite literally) on so many occasions, always steering me in the right direction. I have always cherished your guidance, which has served as a compass for me in all of my pursuits. You repeatedly urged me to work on this textbook ("write the book!", you would say so often), with full confidence that it would be appreciated by students around the world. I will forever rely on the life lessons that you have taught me and the values that you have instilled in me. I love you.

To Larry,

By inspiring me to pursue a career in organic chemistry instruction, you served as the spark for the creation of this book. You showed me that any subject can be fascinating (even organic chemistry!) when presented by a masterful teacher. Your mentorship and friendship have profoundly shaped the course of my life, and I hope that this book will always serve as a source of pride and as a reminder of the impact you've had on your students.

To my wife, Vered,

This book would not have been possible without your partnership. As I worked for years in my office, you shouldered all of our life responsibilities, including taking care of all of the needs of our five amazing children. This book is our collective accomplishment and will forever serve as a testament of your constant support that I have come to depend on for everything in life. You are my rock, my partner, and my best friend. I love you.

David Klein

First and foremost, I want to thank my students for making my job the greatest job in the world. My contributions to this textbook have come directly from the work my students and I have done together over the past 29 years. Thank you to my graduate advisor, Mike Jung, for providing a supportive environment and for believing in an ADHD student who failed her first organic synthesis exam in grad school! Thank you to my mentor, Phil Beauchamp, who is both a passionate educator and an organic chemistry junkie. Thank you to my friends, roommates and lab mates who helped me thrive at UConn and at UCLA. Thank you to all of my Cal Poly Pomona colleagues, department chairs and faculty center directors over the years for helping me build a fulfilling career and a happy home away from home. A giant thank you to my coauthor, David Klein, for his dedication and support and creativity and enthusiasm. Thank you for putting your trust in me, and for giving me the opportunity to help you make a great book even better. The voyage has been both exhausting and exhilarating, and I couldn't have done it without such an amazing partner.

I am so very lucky to be able to share a laugh with so many wonderful people in my life. Thank you to my extended family for their love, encouragement, support, and friendship...and for making me the person that I am today. Thank you to my dad for helping me to set my sights high (and, of course, thanks for putting chemistry in my genes!). Thank you to my mom for always believing in me and for reminding me to never stop exploring. Thank you to my sister, Christine, for always being a step ahead of me so I could see where I should be going, and for including the Starkeys in your travel adventures. Thank you to Mom Starkey for always being there for me. You took me in as a teenager, and you've been my biggest cheerleader and one of my best friends ever since. To Mike, my everything, thank you for a lifetime of love and joy. Your never-ending support made it all possible, and your companionship made it worthwhile. To my kids, Ellie and Andy, thank you for showing me an entirely new level of love and joy, and thank you for putting up with a working mom. I am crazy proud of you both. I hope that you never stop exploring, but always stop to read the plaques! I am profoundly grateful for my wolfpack, because the most important things in life aren't things.

Laurie Starkey

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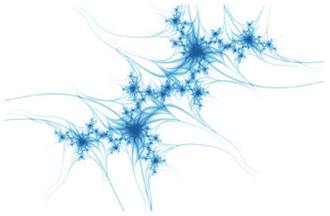

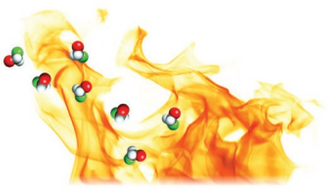

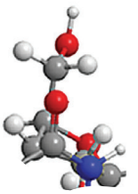

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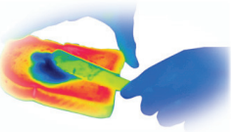

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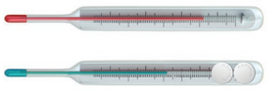

Preface

WHY I WROTE AN ORGANIC CHEMISTRY TEXTBOOK, BY DAVID KLEIN

Students who perform poorly on organic chemistry exams often report having invested countless hours studying. Why do many students have difficulty preparing themselves for organic chemistry exams? Certainly, there are several contributing factors, including inefficient study habits, but perhaps the most dominant factor is *a fundamental disconnect between what students learn in the lecture hall and the tasks expected of them during an exam*. To illustrate the disconnect, consider the following analogy.

Imagine that a prestigious university offers a course entitled "Bike-Riding 101." Throughout the course, physics and engineering professors explain many concepts and principles (for example, how bicycles have been engineered to minimize air resistance). Students invest significant time studying the information that was presented, and on the last day of the course, the final exam consists of riding a bike for a distance of 100 feet. A few students may have innate talents and can accomplish the task without falling. But most students will fall several times, slowly making it to the finish line, bruised and hurt; and many students will not be able to ride for even one second without falling. Why? Because there is a *disconnect* between what the students learned and what they were expected to do for their exam.

Many decades ago, I noticed that a similar disconnect existed in traditional organic chemistry instruction. That is, learning organic chemistry is much like bicycle riding; just as the students in the bike-riding analogy were expected to ride a bike after attending lectures, it was often expected that organic chemistry students would independently develop the necessary skills for solving problems. While a small percentage of students have innate talents and are able to develop the necessary skills independently, most students require guidance. This guidance was not consistently integrated within existing textbooks, prompting me to write the first edition of my textbook, *Organic Chemistry*. The main goal of my text was to employ a skills-based approach to bridge the gap between theory (concepts) and practice (problem-solving skills). The second and third editions further supported this goal by introducing hundreds of additional problems based on the chemical literature, thereby exposing students to exciting, real-world examples of chemical research being conducted in real laboratories. In the fourth edition, the treatment of synthesis was strengthened throughout the text, with a greater focus on retrosynthetic strategies. The phenomenal success of the first four editions has been extremely gratifying because it provided strong evidence that my skills-based approach is indeed effective at bridging the gap between theory and practice.

The new, fifth edition has many exciting improvements (a partial list is provided below), but most exciting is that Professor Laurie Starkey is now a coauthor on the 5th edition. Laurie and I have collaborated together for many years, and we are thrilled to share this new edition with you and your students.

Laurie and I firmly believe that the scientific discipline of organic chemistry is NOT merely a compilation of principles, but rather, it is a disciplined method of thought and analysis. Students must certainly understand the concepts and principles, but more importantly, *students must learn to think like organic chemists* . . . that is, they must learn to become proficient at approaching new situations methodically, based on a repertoire of skills. That is the true essence of organic chemistry, and that must be the primary focus of teaching and learning organic chemistry.

A SKILLS-BASED APPROACH

To address the disconnect in organic chemistry instruction, I have developed a skills-based approach to instruction. The textbook includes all the concepts typically covered in an organic chemistry textbook, complete with conceptual checkpoints that promote mastery of the concepts, but special emphasis is placed on skills development through learning modules called *SkillBuilders*. Each SkillBuilder contains three parts:

Learn the Skill contains a solved problem that demonstrates a particular skill.

Practice the Skill includes numerous problems (similar to the solved problem in Learn the Skill) that give students valuable opportunities to practice and master the skill.

Apply the Skill gives the student an opportunity to apply the skill to solve real-world problems (as reported in the chemical literature). Apply the Skill problems include conceptual, cumulative, and applied problems that encourage students to think outside of the box. Sometimes problems that foreshadow concepts introduced in later chapters are also included.

At the end of each SkillBuilder, a *Need More Practice?* note suggests end-of-chapter problems that students can work further to practice the skill.

The SkillBuilder approach provides students with a greater opportunity to develop proficiency in the key skills necessary to succeed in organic chemistry. Certainly, not all necessary skills can be covered in a textbook. However, there are certain skills that are fundamental to all other skills.

As an example, resonance structures are used repeatedly throughout the course, and students must become masters of resonance structures early in the course. Therefore, a significant portion of Chapter 2 is devoted to pattern-recognition for drawing resonance structures. Rather than just providing a list of rules and then a few follow-up problems, the SkillBuilder approach provides students with a series of practical skills, each of which must be mastered in sequence. Each skill is reinforced with numerous

practice problems. The sequence of skills is designed to foster and develop proficiency in drawing resonance structures.

The skills-based approach to organic chemistry instruction is a unique approach. Certainly, other textbooks contain tips for problem solving, but no other textbook consistently presents skills development as the primary vehicle for instruction.

WHAT'S NEW IN THIS EDITION

Coauthor Laurie Starkey

Laurie has been teaching organic chemistry lecture and laboratory courses at California State Polytechnic University, Pomona (aka Cal Poly Pomona) since 1996. She authored *Introduction to Strategies for Organic Synthesis*, a textbook for senior undergraduate and beginning graduate students, and she contributed to the third and fourth editions of David Klein's *Organic Chemistry*. Laurie is excited to bring these experiences to her collaboration with David, as a coauthor on the fifth edition. After so many years of working closely with a diverse student population, she has developed many successful approaches to teaching various topics, and these have been infused throughout the fifth edition. As an enthusiastic user of the Klein textbook for five years, Laurie was also able to identify potential SkillBuilder revisions, opportunities for improved clarity or efficiency, and improvements to the way certain chapters are organized.

A Focus on Student Motivation

Organic chemistry is a tough subject, and the struggle is real. For many high-achieving students, this course is the first major challenge they have faced in their entire academic career. In addition to the sheer volume of content and the required breakneck pace, students are challenged by the novelty and cumulative nature of the material and the requirement for spatial awareness. They are learning an entirely new language to solve problems without plugging numbers into random equations, and the answers cannot be simply memorized and regurgitated and then forgotten. And so, as with learning any difficult skill, the learner must stumble and must make mistakes. This is a necessary part of the learning process, and *all growth involves discomfort*.

No one knows how a given student will respond when they face an obstacle, but is there anything we can do to help them persist? Indeed, there is! A *motivated* student is more likely to keep working on a challenging problem, put in the required hours, and bounce back after a setback. The desire to pass the class is certainly an extrinsic motivator, but there are concrete ways to increase the student's intrinsic motivation. The best way to motivate students is to illustrate the purpose and relevance of the course content. As such, the fifth edition of *Organic Chemistry* is infused with hundreds of new visual "hooks" that tie into the students' majors, the world around them, and everyday life. If the student is interested in the course, they will be more motivated to do the coursework. For some of these students, that interest might develop into a lifelong passion, like it did for their professor! There are two additional factors that are key to motivating learners: encouraging a growth mindset and promoting a sense of belonging. The student-friendly language and the skill-building approach already reinforces these attributes. The fifth edition has also incorporated study tips, mnemonic devices, pronunciation guides, visual representations of information, highlights of people and careers, inclusive applications, and a supportive tone throughout.

Peer Review

Peer review has played a very strong role in the development of the previous editions of *Organic Chemistry*. The manuscripts for the prior editions were reviewed by several hundred professors and several thousand students! In preparing the fifth edition, peer review has continued to play a prominent role. We have received a tremendous amount of feedback from faculty and input from the market, including surveys, class tests, diary reviews, and phone interviews. All of this input has been carefully evaluated and has been instrumental in identifying revisions for the fifth edition.

New to the Fifth Edition

✓ **Over 400 new images** have been added to visually represent information, provide a molecular model kit image, or to point out the purpose and relevance of the course content. Nearly every SkillBuilder in 5e now has an image with a caption to accompany the *Apply the Skill* literature-based problem.

✓ The following **SkillBuilders** are either new or have been significantly revised.

- Chapter 1 – Redesigned SkillBuilders 1.1 (identifying rather than drawing constitutional isomers) and 1.2 (added a systematic approach to drawing Lewis structures based on filling octets)
- Chapter 2 – Drawing 3D Structures (**NEW**)
- Chapter 2 – Identifying Lone Pairs on Oxygen and Nitrogen Atoms (consolidated, more efficient, improved problem-solving strategies)
- Chapter 5 – Identifying Chiral Molecules (**NEW**)
- Chapter 5 – Interconverting Bond-Line Drawings and Fischer Projections (**NEW**)
- Chapter 5 – Drawing Stereoisomers (**NEW**)
- Chapter 7 – Drawing the Mechanism and Predicting the Product of an S_N1 Process (**NEW**)
- Chapter 7 – Revised SkillBuilder 7.1 to include drawing the mechanism in addition to predicting the product of an S_N2 process, and to introduce a stepwise problem-solving approach.
- Chapter 7 – Revised SkillBuilder 7.7 Predicting the Products of Substitution and Elimination Reactions to include a problem-solving approach, based on a decision tree.
- Chapter 8 – Revised SkillBuilder 8.3 Predicting the Product and Drawing a Mechanism for an Acid-Catalyzed Hydration (expanded to include predicting the product)
- Chapter 14 – Revised SkillBuilder 14.1 Analyzing an IR Spectrum by introducing a novel, five-step, systematic approach to interpreting an IR spectrum.

- Chapter 14 – Predicting Fragmentation Patterns and Analyzing Fragments in a Mass Spectrum (**NEW**)
- Chapter 15 – Revised SkillBuilder 15.3 Predicting Chemical Shifts by introducing a novel, simple calculation for estimating chemical shifts.
- Chapter 15 – Revised SkillBuilder 15.8 Analyzing a ^{1}H NMR Spectrum by introducing a novel, systematic, five-step approach to solving a proton NMR spectrum.
- Chapter 21 – Expanded SkillBuilders 21.1 (Drawing Enolates) and 21.2 (Predicting the Products of an Aldol Addition) by including the drawing of mechanisms.

✓ **Complete Redesign of Chapter 5 Stereoisomerism**

- Two new sections: Chirality and Chiral Centers (5.2) and Stereoisomeric Relationships and Physical Properties (5.6)
- Two new SkillBuilders: Identifying Chiral Molecules and Drawing Fischer Projections
- Revised and simplified SkillBuilder 5.4 Drawing an Enantiomer – two problem-solving options are presented
- Simplified assigning *R/S* configurations (#4 on dash, #4 on wedge, #4 in plane, Fischer projections) and provided multiple problem-solving options
- Presented an application of polarized light in photography, with images
- Expanded coverage of enantiomeric excess, including several graphics to illustrate the composition of various mixtures

✓ **Complete Redesign of Chapter 20 Carboxylic Acids and Their Derivatives**

- The material has been completely reorganized to reflect a mechanism-based approach:
  1. Carboxylic acids (nomenclature, properties and preparation)
  2. Nomenclature of carboxylic acid derivatives
  3. Introduction to Acyl Substitution reactions, with an emphasis on acid- vs. base-catalyzed mechanisms.
  4. Irreversible reactions (review of hydride and Grignard nucleophiles)
  5. Hydrolysis of carboxylic acid derivatives
  6. Reactivity of carboxylic acid derivatives (with a new subsection on leaving group abilities)
  7. Preparation of carboxylic acid derivatives
  8. Preparation and reactions of nitriles
  9. Selective reagents [DIBAL-H, $LiAl(OR)_3H$, R_2CuLi]
  10. Synthesis strategies
  11. Spectroscopy
- Additional revisions: Expanded IUPAC coverage to include oxo substituents, and to provide more examples of systematic names; Added a MolyMod molecular model to illustrate delocalized electrons in the resonance hybrid of acetic acid; Added a discussion of reactivity of ketones vs. esters and the selectivity of $NaBH_4$; Micelle material moved here from Chapter 1 to be with saponification reaction; Streamlined the Review of Reactions at the end of the chapter; Fifteen new problems added (research-based predict the product, research-based provide the reagent, determine the direction of an acyl substitution equilibrium).

✓ **New Sections**, and **Mechanism-Based Reorganizations**

- Chapter 3 – New section: **Acids and Bases in Living Systems** to introduce pH, indicators, Henderson-Hasselbalch equation, and various functional groups at physiological pH (amines, carboxylic acids and amino acids)
- Chapter 7 – New section: **Competing Pathways: S_N2 vs. E2**
- **Chapter 9 – Reorganized material** to place Acidity of Alkynes and Alkylation of Terminal Alkynes to be consecutive and towards the end of the chapter.
- Chapter 11 – New section: **Natural Product Synthesis** introduces the field, explores the motivating forces and the history of organic synthesis, and expands on the existing BioLink to tell the remarkable story of the synthesis of Vitamin B_{12}.
- Chapter 14 – New section: **Characteristic Signals of Functional Groups**
- Chapter 14 – New section: **Analyzing Isotopes**, with new pie charts to represent the abundance of Br and Cl isotopes, and a reduced focus on the M+1 peak (SkillBuilder 14.3 in the fourth edition has been removed)
- **Chapter 19 – Reorganized material** to begin with irreversible nucleophilic additions (a review of hydride and Grignard nucleophiles, followed by Wittig reagents) before moving into reversible reactions (oxygen and nitrogen nucleophiles). The distinction between reversible and irreversible reactions is presented in Section 19.4 "Introduction to Nucleophilic Addition Reactions."
- Chapter 19 – New section: **Reduction of Aldehydes and Ketones to Alkanes** to review prior content (Clemmenson) and introduce additional methods (reduction of thioacetals and Wolff-Kishner).
- **Chapter 21 – Reorganized material** to introduce alpha alkylation as the first enolate reaction (simple backside attack). Also, the acetoacetic ester synthesis and malonic ester synthesis have been relocated to the Synthesis Strategies section, and these topics are now used to introduce the concept of synthetic equivalents.
- Chapter 23 – New section: **Asymmetric Catalysis** introduces Wilkinson's catalyst and shows the catalytic cycle for the hydrogenation reaction

✓ **Expanded and redesigned content in every chapter**

Throughout the text, figures and artwork have been improved with annotations and color. Explanations and SkillBuilder instructions have been clarified. In many cases, the narrative has been expanded and examples have been added, but there were also opportunities to streamline certain material for a more efficient presentation. A detailed list of changes for each chapter can be found online in WileyPLUS

✓ **Global revisions and features**:

- Revised pK_a of H_3O^+ (0.0) and H_2O (14.0)
- Expanded IUPAC rules and examples, added problems with multiple functional groups
- Revised labels for all proton transfer steps in mechanisms to read as *Protonate* or *Deprotonate*
- SkillBuilders are now listed in the Table of Contents at the beginning of each chapter
- Green Chemistry icon is used to highlight relevant content
- "Hello my name is…" beaker images to identify name reactions
- Introduced a common pattern observed in acid-catalyzed reaction mechanisms: P.A.D. (**P**rotonate, Nucleophilic **A**ttack, **D**eprotonate). The P.A.D. pattern applies to acid-catalyzed hydration of alkenes and alkynes, acid-catalyzed epoxide ring opening reactions (with water or ROH), and formation of a hydrate or a hemiacetal.
- Added a discussion of study strategies in Chapter 8 by providing examples of effective flash cards. Three flash cards can be prepared for a given reaction (missing product, missing reagents, missing substrate). In later chapters, students are reminded of the study strategy, and examples of flash cards are given.

TEXT ORGANIZATION

The sequence of chapters and topics in *Organic Chemistry*, 5e does not differ markedly from that of other organic chemistry textbooks. Indeed, the topics are presented in the traditional order, based on functional groups (alkenes, alkynes, alcohols, ethers, aldehydes and ketones, carboxylic acid derivatives, etc.). Despite this traditional order, a strong emphasis is placed on mechanisms, with a focus on pattern recognition to illustrate the similarities between reactions that would otherwise appear unrelated. No shortcuts were taken in any of the mechanisms. All steps are clearly illustrated and annotated, including all proton transfer steps.

Two chapters (6 and 11) are devoted almost entirely to skill development and are generally not found in other textbooks. Chapter 6, Chemical Reactivity and Mechanisms, emphasizes skills that are necessary for drawing mechanisms, while Chapter 11, Synthesis, prepares the students for proposing syntheses. These two chapters are strategically positioned within the traditional order described above and can be assigned to the students for independent study. That is, these two chapters do not need to be covered during precious lecture hours, but can be, if so desired.

The traditional order allows instructors to adopt the skills-based approach without having to change their lecture notes or methods. For this reason, the spectroscopy chapters (Chapters 14 and 15) were written to be stand-alone and portable, so that instructors can cover these chapters in any order desired. In fact, five of the chapters (Chapters 2, 3, 7, 12, and 13) that precede the spectroscopy chapters include end-of-chapter spectroscopy problems, for those students who have covered spectroscopy earlier. Spectroscopy coverage also appears in subsequent functional group chapters, specifically Chapter 17 (Aromatic Compounds), Chapter 19 (Aldehydes and Ketones), Chapter 20 (Carboxylic Acids and Their Derivatives), Chapter 22 (Amines), Chapter 24 (Carbohydrates), and Chapter 25 (Amino Acids, Peptides, and Proteins).

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- SkillBuilders can be assigned as a whole, so students are presented with the complete learning module (Learn the Skill, Practice the Skill, Apply the Skill with literature citation and a relevant visual hook)

- Students should not spend more time learning how to use a drawing tool than they do learning organic chemistry. For the 5th edition, the focus is on student success, with intuitive drawing questions powered by Alchemie, a fully accessible, auto-gradable experience designed for chemistry education. These tools provide a seamless drawing experience that allows students to focus on chemistry content rather than trying to get arrows and bond placement to work. These drawing questions provide immediate feedback as students explore content, gaining the deeper connections needed for long-lasting learning.
- Clear instructions are provided, and no unnecessary drawing is required. In most cases, predict-the-product problems provide a copy of the starting material in the sketch box, so students can focus on the reactive functional group(s).
- Synthesis problems are open-ended to better reflect classroom assessments.
- Advanced problems are scaffolded with guided inquiry to model problem-solving. For example, challenging synthesis problems begin with a retrosynthetic analysis, and mechanism problems might begin with an overview before moving into arrow-pushing.
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In addition to providing students with an exceptional opportunity for practice and formative assessment, WileyPLUS offers engaging videos and interactive graphics. David Klein created over 100 lightboard videos to cover each of the boxed (numbered) mechanisms appearing in the text. In concise videos (5–10 minutes in duration), each step of the mechanism is described in detail, and the student sees the entire mechanism unfolding in a step-by-step fashion. The author shows how to draw the resulting intermediate and how to decide what happens next when drawing the mechanism. The reason for each step is explained, and experimental observations (regiochemical and stereochemical) are justified. The function of each reagent is explained, and curved arrows are drawn one at a time, with a discussion of how each arrow should be drawn. These videos bring to life the dynamic nature of a reaction mechanism, and they are designed to foster a solid grasp of the skills necessary for drawing mechanisms. For the fifth edition, and with the same careful attention to detail, David created a lightboard video to accompany every SkillBuilder (approximately 200) throughout the text. By modeling problem-solving, these videos provide students with a step-by-step explanation of the skills that are foundational to the study of organic chemistry. In total, there are now 300 lightboard videos, covering all mechanisms and all SkillBuilders in the text.

ADDITIONAL INSTRUCTOR RESOURCES

Testbank Revised for this edition by Ashley Steelman, University of Kentucky

PowerPoint Lecture Slides and Clicker Questions Revised for this edition by Dr. Todd J. Eckroat, Penn State Behrend and Dr. Mike Cross, Snow College

STUDENT RESOURCES

Student Study Guide and Solutions Manual Authored by David Klein. The fifth edition of the *Student Study Guide and Solutions Manual* to accompany *Organic Chemistry, 5e* contains:

- More detailed explanations within the solutions, with hundreds of new images
- Concept Review Exercises
- SkillBuilder Review Exercises
- Reaction Review Exercises
- Mechanism Review Exercises
- A list of new reagents for each chapter, with a description of their function.
- A list of "Common Mistakes to Avoid" in every chapter.

Molecular Visions™ Model Kit To support the learning of organic chemistry concepts and allow students the tactile experience of manipulating physical models, we offer a molecular modeling kit from the Darling Company. The model kit can be bundled with the textbook or purchased stand alone.

CONTRIBUTORS TO *ORGANIC CHEMISTRY, 5E*

We owe special thanks to all of our contributors over the years for their collaboration, hard work, and creativity. Several of the new BioLinks and WorldLinks application boxes throughout the fifth edition were written by Ron Swisher, Oregon Institute of Technology.

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Despite our best efforts, as well as the best efforts of the reviewers, accuracy checkers, and class testers, errors may still exist. We take full responsibility for any such errors and would encourage those using our textbook to contact us with any errors that you may find.

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A Review of General Chemistry

ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

DID YOU EVER **WONDER...**
what causes lightning?

Believe it or not, the answer to this question is still the subject of debate (that's right... scientists have not yet figured out everything, contrary to popular belief). There are various theories that attempt to explain what causes the buildup of electric charge in clouds. One thing is clear, though—lightning involves a flow of electrons. By studying the nature of electrons and how electrons flow, it is possible to control where lightning will strike. A tall building can be protected by installing a lightning rod (a tall metal column at the top of the building) that attracts any nearby lightning bolt, thereby preventing a direct strike on the building itself. The lightning rod on the top of the Empire State Building is struck over a hundred times each year.

Just as scientists have discovered how to direct electrons in a bolt of lightning, chemists have also discovered how to direct electrons in chemical reactions. We will soon see that although organic chemistry is defined as the study of compounds containing carbon atoms, its true essence is actually the study of electrons, not atoms. Rather than thinking of reactions in terms of the motion of atoms, we must

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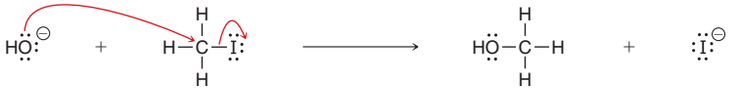
recognize that *reactions occur as a result of the motion of electrons*. For example, in the following reaction the curved arrows represent the motion, or flow, of electrons as one bond breaks and a new bond forms. This flow of electrons causes the chemical change shown:

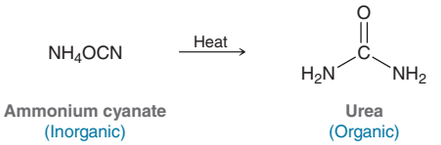


Throughout this course, we will learn how, when, and why electrons flow during reactions. We will learn about the barriers that prevent electrons from flowing, and we will learn how to overcome those barriers. In short, we will study the behavioral patterns of electrons, enabling us to predict, and even control, the outcomes of chemical reactions.

This chapter reviews some relevant concepts from your general chemistry course that should be familiar to you. Specifically, we will focus on the central role of electrons in forming bonds and influencing molecular properties.

1.1 Introduction to Organic Chemistry

In the early nineteenth century, scientists classified all known compounds into two categories: *Organic compounds* were derived from living organisms (plants and animals), while *inorganic compounds* were derived from nonliving sources (minerals and gases). This distinction was fueled by the observation that organic compounds seemed to possess different properties than inorganic compounds. Organic compounds were often difficult to isolate and purify, and upon heating, they decomposed more readily than inorganic compounds. To explain these curious observations, many scientists subscribed to a belief that compounds obtained from living sources possessed a special "vital force" that inorganic compounds lacked. This notion, called vitalism, stipulated that it should be impossible to convert inorganic compounds into organic compounds without the introduction of an outside vital force. Vitalism was challenged in 1828 when German chemist Friedrich Wöhler demonstrated the conversion of ammonium cyanate (a known inorganic salt) into urea, a known organic compound found in urine:



Over the decades that followed, other examples were found, and the concept of vitalism was gradually rejected. The downfall of vitalism shattered the original distinction between organic and inorganic compounds, and a new definition emerged. Specifically, **organic** compounds became defined as those compounds containing carbon atoms, while **inorganic** compounds generally were defined as those compounds lacking carbon atoms. There are a few exceptions to this general definition. For example, ammonium cyanate (seen on this page) is still classified as inorganic, despite the presence of a carbon atom. Some other carbon-containing compounds that are considered to be inorganic are carbon dioxide (CO_2), sodium carbonate (Na_2CO_3), and potassium cyanide (KCN).

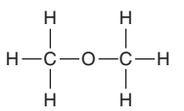
Organic chemistry occupies a central role in the world around us, as we are surrounded by organic compounds. The food that we eat and the clothes that we wear are comprised of organic compounds. Our ability to smell odors or see colors results from the behavior of organic compounds. Pharmaceuticals, bug sprays, paints, adhesives, and plastics are all made from organic compounds. In fact, our bodies are constructed mostly from organic compounds (DNA, RNA, proteins, etc.), and the responses of our bodies to pharmaceuticals are the results of reactions guided by the principles of organic chemistry. A deep understanding of those principles enables the design of new drugs that fight disease and improve the overall quality of life and longevity. Accordingly, it is not surprising that organic chemistry is required knowledge for anyone entering the health professions.

Organic Food vs. Organic Chemistry

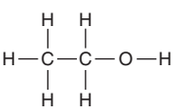
You have undoubtedly encountered the term "organic" before taking this course. Food that is labeled "organic" is grown and processed according to defined standards. For example, organic *foods* contain only natural additives, and organic *farming* restricts the use of certain pesticides and fertilizers. Now that you have learned the definition of organic *chemistry*, you can see that the word "organic" depends heavily on context. Afterall, many pesticides are in fact organic compounds! With this newly acquired lens, you will find that organic compounds, products, and materials can be found in every part of our lives. Many organic materials are made by nature, and others are synthetic (made by humans), but they are all part of the story of organic chemistry. Perhaps you can identify some examples of organic chemistry in the photos below? You certainly have an exciting journey ahead, as we explore this fascinating world together. In the meantime, visit the Student Solutions Manual to learn more about what can be found in these photos.

1.2 Constitutional Isomerism

As we explore organic compounds in the following chapters, an extraordinary variety of chemical and physical properties will be revealed. What makes every organic compound unique is not only the number and types of atoms from which it is composed (its **molecular formula**), but the way in which the atoms are connected. As an example, consider the following two compounds:



Dimethyl ether
✓ Boiling point = −23°C
✓ Gas at room temp.
✓ Found in a can of spray paint



Ethanol
✓ Boiling point = 78.4°C
✓ Liquid at room temp.
✓ Found in a bottle of wine

These compounds have the same molecular formula (C_2H_6O), yet they differ from each other in the way the atoms are connected—that is, they differ in their constitution. As a result, they are called constitutional isomers. **Constitutional isomers** have different physical properties and different names. The first compound is a colorless gas used as an aerosol spray propellant, while the second compound is a clear liquid, commonly referred to as "alcohol," found in alcoholic beverages.

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