

INTRODUCTION TO  
ORGANIC CHEMISTRY



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# INTRODUCTION TO ORGANIC CHEMISTRY

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Beloit College



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The publisher and author have gone to extreme measures in attempting to ensure the publication of an error-free text. The manuscript, galleys, and page proofs have been carefully checked by the author, the editors, and a battery of reviewers. While we realize that a 100% error-free text may not be humanly possible, Brown's *Introduction to Organic Chemistry* is very close. Confirmed in this belief, we are offering \$5.00 for any first-time error you may find. (Note that we will only pay for each error the first time it is brought to our attention.) Please write to John Vondeling, Publisher.

## Some Important Organic Functional Groups

Functional Group*		Functional Group*	
Example	IUPAC Name	Example	IUPAC Name
$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}=\text{C}-\text{O}-\text{C}-\text{O} \\ \parallel \\ \text{O} \end{array}$	Ethanoic anhydride (Acetic anhydride)	$\text{CH}_3\text{COCH}_3$	Acetone
$\begin{array}{c} \text{O} \\ \parallel \\ \text{O}=\text{C}-\text{Cl} \end{array}$	Ethanoic chloride (Acetyl chloride)	$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol (Ethyl alcohol)
$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol (Ethyl alcohol)	$\text{CH}_3\text{CHO}$	Ethanal (Acetaldehyde)
$\text{CH}_3\text{CHO}$	Ethanal (Acetaldehyde)	$\text{CH}_3\text{CH}_3$	Ethane
$\text{CH}_3\text{CH}_3$	Ethane	$\text{CH}_2=\text{CH}_2$	Ethene (Ethylene)
$\text{CH}_2=\text{CH}_2$	Ethene (Ethylene)	$\text{HC}\equiv\text{CH}$	Ethyne (Acetylene)
$\text{HC}\equiv\text{CH}$	Ethyne (Acetylene)	$\text{CH}_3\text{CNH}_2$	Ethanamide (Acetamide)
$\text{CH}_3\text{CNH}_2$	Ethanamide (Acetamide)	$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethylamine
$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethylamine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	Diethylamine
$(\text{CH}_3\text{CH}_2)_2\text{NH}$	Diethylamine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	Triethylamine
$(\text{CH}_3\text{CH}_2)_3\text{N}$	Triethylamine		

\*Where bonds to an atom are not specified, the atom is assumed to be bonded to one or more carbon or hydrogen atoms in the rest of the molecule.



## Functional Groups Preparation—Master Table

### Target Functional Group

Starting from	Acid anhydride	Acid chloride	Alcohol	Aldehyde	Alkane	Alkene	Alkyl-arene	Alkyl-halide	Amide	Amine	Arene	Aryl halide	Carboxylic acid	Epoxide	Ester	Ether	Glycol	Ketone	Nitroarene
	Acid anhydride								14.5B				14.3B		14.4B				
	Acid chloride								14.5A				14.3A		14.4A			9.7C	
	Alcohol			7.4F		7.4E	9.7D	7.4D					7.4F		13.6	8.9		7.4F	
	Aldehyde		11.5, 11.10							11.10C			11.9A						
	Alkane							2.9B											
	Alkene		4.3B		4.6		9.7D	4.3A						7.6B			4.5B		
	Alkylarene												9.5						
	Alkyl halide		8.3, 11.5			8.7	9.7C			8.2			11.5B			8.9			
	Amide									14.7B			14.3D						
	Amine							8.2	14.5										
	Arene						9.7C					9.7A	11.5B						9.7B
	Aryl halide																		
	Carboxylic acid	13.7	13.5												13.6				
	Epoxide		11.5B														7.7A		
	Ester		14.7A						14.5C				14.3C						
	Ether																		
	Glycol																		
	Ketone		11.5, 11.10							11.10C			11.9B						
	Nitroarene									9.7B		10.6							

**New C—C bonds are formed by**

Aldol reactions	15.2
Alkylation of arenes	9.7C, D
Claissen condensations	15.3
Dieckman condensations	15.3
Friedel-Crafts acylations	9.7C
Friedel-Crafts alkylation	9.7C
Grignard reactions	11.5
Polymerization of alkenes	4.7

**To form new C—O bonds of**

Acetals	11.6B, 12.4A
Alcohols	4.3B, 8.2
Carboxylic acids	9.5, 11.9B, 14.3
Epoxides	7.6B
Esters	13.6, 14.4
Ethers	8.9
Glycols	4.5B

### To form new C—N bonds of

Amides	14.5A, 14.5B, 14.5C
Amines	8.2
Imines	11.7
Nitroarenes	9.7B



# INTRODUCTION TO ORGANIC CHEMISTRY

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Introduction to organic chemistry /





***To Carolyn,  
with whom  
life is a joy***



# Preface

## The Audience

This book provides an introduction to organic chemistry for students aiming toward careers in science—not necessarily chemistry—that require a grounding in organic chemistry. For this reason, I make a special effort throughout this text to show the interrelation between organic chemistry and these areas, particularly the biological and health sciences. I show that organic chemistry is a tool for these many disciplines and that organic compounds, both natural and synthetic, are all around—in pharmaceuticals, plastics, fibers, agrochemicals, surface coatings, toiletry preparations and cosmetics, food additives, adhesives, and elastomers. Further, I hope to show students that organic chemistry is a dynamic and ever-expanding area of science waiting openly for those who are prepared, both by training and inquisitive nature, to ask questions and to explore.

## Organization: An Overview

Chapters 1–11 and 13–15 lay a foundation for studying organic chemistry by covering the structures and typical reactions of the important classes of organic compounds: alkanes and cycloalkanes; alkenes; alcohols, ethers, and thiols; benzene and its derivatives; amines; aldehydes and ketones; and finally carboxylic acids and their derivatives. Chapters 12 and 16–19 present a brief introduction to the organic chemistry of biochemical compounds: carbohydrates, lipids, amino acids and proteins, and nucleic acids. Chapters 20 and 21 introduce  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and IR spectroscopy. Discussions of spectroscopy require no more background than what students receive in general chemistry. These chapters are free-standing and can be covered in any order appropriate to a particular course. In the end-of-chapter problems of each functional group chapter, I give reference to the appropriate end-of-chapter problems in the spectroscopy chapters.

## Chapter-by-Chapter

Chapter 1 begins with a review of the electronic structure of atoms and molecules, and use of the VSEPR model to predict shapes of molecules and polyatomic ions. It is followed by an introduction to the hydroxyl, carbonyl, and carboxyl groups,

the functional groups encountered most frequently in Chapters 1–19. The theory of resonance is introduced midway through Chapter 1, and with it the use of curved arrows and electron pushing. The knowledge of resonance theory combined with a facility for pushing electrons gives students two powerful tools for writing reaction mechanisms and understanding chemical reactivity. Chapter 1 concludes with an introduction to the valence bond description of covalent bonding.

Chapter 2 opens with a description of the structure, nomenclature, and conformations of alkanes and cycloalkanes. Beginning here and continuing throughout the text, a clear distinction is made between IUPAC and common names. Where names are introduced, the IUPAC name is given and the common name or names, where appropriate, follow in parentheses. The IUPAC system is introduced in Section 2.3 through the naming of alkanes, and in Section 2.5, the IUPAC system is presented as a general system of nomenclature. Halogenation of alkanes is presented, with concentration on its regioselectivity.

Structure, nomenclature, and physical properties of alkenes and alkynes are presented in Chapter 3. Chapter 4 opens with an introduction to chemical energetics and the concept of a reaction mechanism. Reactions of alkenes are organized in the following order: electrophilic additions, oxidation, reduction, and addition polymerization. The concepts of regioselectivity and stereoselectivity are introduced in the context of electrophilic additions.

Chapter 5 begins with a review of constitutional and *cis-trans*/*E,Z* isomerism, and then introduces the concepts of chirality, enantiomerism, and diastereomerism. Students are then challenged to use these concepts to develop a deeper understanding of the stereochemistry of electrophilic addition reactions of alkenes.

Contained in Chapter 6 is a general introduction to acid-base chemistry with emphasis on qualitative determination of the position of equilibrium in acid-base reactions. Students are given tools to answer questions such as “Will phenol dissolve in aqueous sodium bicarbonate?” A correlation between acidity and electronegativity of the atom bonded to hydrogen is given in this chapter. Correlations between acidity and structure through inductive and resonance effects are taken up later in the discussion of phenols, carboxylic acids,  $\alpha$ -hydrogens, and amino acids.

Chapter 7 continues the theme of relationships between structure and reactivity by considering the chemistry of alcohols. The concepts of one-step and two-step nucleophilic substitutions along with  $S_N1$  and  $S_N2$  terminology are introduced in a preliminary way with the reactions of alcohols with HX. These concepts are then reinforced and expanded upon in the following chapter on Alkyl Halides.

I present nucleophilic substitution in Chapter 8 after the discussion of alkenes, stereochemistry, and alcohols because, by this stage in the course, students have a good grounding in the structure of organic molecules, the theory of resonance, electron pushing, and reaction mechanisms. Nucleophilic substitution and  $\beta$ -elimination then become a vehicle for integration of previously covered chemistry into a larger pattern.

Chapter 9 opens with the structure and nomenclature of aromatic compounds and several important heterocyclic aromatic compounds. I introduce students to the unique properties of aromatic rings through the acid-base properties of phenols—why phenols are more acidic than alcohols. The mechanism for electrophilic aromatic substitution, including the theory of directing effects, is then presented in detail.

The chemistry of amines (Chapter 10) follows the chemistry of alcohols and phenols, and begins with the basicity of amines. At this point, students can appre-



ciate relationships between structure and relative basicities of aliphatic and aromatic amines. The chapter concludes with the synthetic usefulness of arenediazonium salts.

In Chapter 11, the reactions of aldehydes and ketones are grouped by type of nucleophile adding to form a tetrahedral carbonyl addition product: carbon nucleophiles, oxygen nucleophiles, and nitrogen nucleophiles. The acidity of  $\alpha$ -hydrogens is then introduced along with keto-enol tautomerism, followed by oxidation and reduction of aldehydes and ketones.

The chemistry of carbohydrates in Chapter 12 is built on the chemistry of two functional groups, namely the hydroxyl group of alcohols (Chapter 7) and the carbonyl group of aldehydes and ketones (Chapter 11). For this reason I present the chemistry of carbohydrates immediately following the chemistry of aldehydes and ketones.

Chapters 13 and 14 together present the chemistry of carboxylic acids and their functional derivatives. Contained in Chapter 14 is a discussion of step-growth organic polymers.

Grouped in Chapter 15 are carbon-carbon bond-forming reactions based on the nucleophilic character of enolate anions. First is the aldol reaction followed by the Claisen and related condensations. The chapter concludes with a discussion of conversion of acetyl-CoA to isopentenyl pyrophosphate.

In Chapter 16, the properties of lipids begins with a discussion of fatty acids, natural soaps, and synthetic detergents followed by prostaglandins and steroids. There is a brief discussion of the biosynthesis of steroids, which builds on the synthesis of isopentenyl pyrophosphate from Chapter 15. The chapter concludes with a discussion of phospholipids and the fat-soluble vitamins.

Chapter 17 gives considerable attention to the acid-base properties of amino acids and then continues with an introduction to primary, secondary, tertiary, and quaternary structure of polypeptides.

Emphasis in Chapter 18 is on primary, secondary, and tertiary structure of DNA with only a brief introduction to the structure of ribonucleic acids. Following the discussion of the genetic code, there is an introduction to the concepts of DNA sequencing, including DNA fingerprinting.

Chapter 19 presents a discussion of the organic chemistry of two key metabolic pathways, namely  $\beta$ -oxidation of fatty acids and glycolysis. It is my purpose to show that reactions of these pathways are biochemical equivalents of organic functional group reactions we have already studied in detail.

Chapter 20 presents the fundamentals of both  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopy, while IR spectroscopy is covered in Chapter 21. These chapters are free-standing and can be used in other orders as appropriate to a particular course.

### Synthetic Organic Chemistry

Synthesis is what organic chemists do best; synthesis of plastics, textile fibers, pharmaceuticals, agrochemicals, and so on. Yet few if any students in a one-term organic course will have occasion to practice synthetic organic methodology. Their concern is, rather, understanding functional-group interconversions as they apply to other areas of professional interest. Therein lies a dilemma for a one-term text—to synthesize or not to synthesize? My balance is guided by two factors. First, I use problems of synthesis to reinforce the essential chemistry of functional groups; call it drill, if you like. Second, I use synthesis to demonstrate the application of organic chemistry to the creation of plastics, textile fibers, pharmaceuticals, agrochemicals,

and so on. I also present a unique overview of the methods of functional group interconversion in the front inside cover of the book: Functional Groups Preparation—Master Table. Listed here are references to all methods of preparation of each functional group presented in this text. The table shows, for example, that alcohols are prepared from alkenes (Section 4.3B), epoxides (Sections 7.7 and 11.5B), alkyl halides (Sections 8.3 and 11.5), aldehydes and ketones (Sections 11.5 and 11.10), carboxylic acids (Section 13.5), and esters (Section 14.7A).

## Special Features

### Full-Color Art Program

One of the most distinctive features of this text is its visual impact. The text's extensive full-color art program includes over 200 pieces of art by professional artists John and Bette Woolsey.

### Photo Art

Photos, conceived and developed for this text, show organic chemistry as it occurs in the laboratory and in everyday life, and depict the natural sources of many organic compounds.

### Stereoviews

A collection of stereoviews has been prepared for this text, each chosen to reinforce the concept of organic chemistry as a three-dimensional science. Each copy of the text is equipped with a pair of stereoglasses for easy viewing. Stereoart is indicated by the following icon: **STEREO**



### Chemical Connections Boxes

These boxes illustrate applications of organic chemistry to everyday settings. Some of these essays are "Capsaicin, for Those Who Like It Hot" (Chapter 9), "Poison Dart Frogs of South America" (Chapter 10), and "DNA Fingerprinting" (Chapter 18).

### In-Chapter Examples

There are an abundance of in-chapter examples, each with a detailed solution. Following each in-chapter example is a comparable practice problem designed to give students the opportunity to solve a related problem.

### End-of-Chapter Problems

There are plentiful end-of-chapter problems. All problems are categorized by topic. A tetrahedral icon indicates an applied problem, and a number set in blue indicates a more challenging problem.

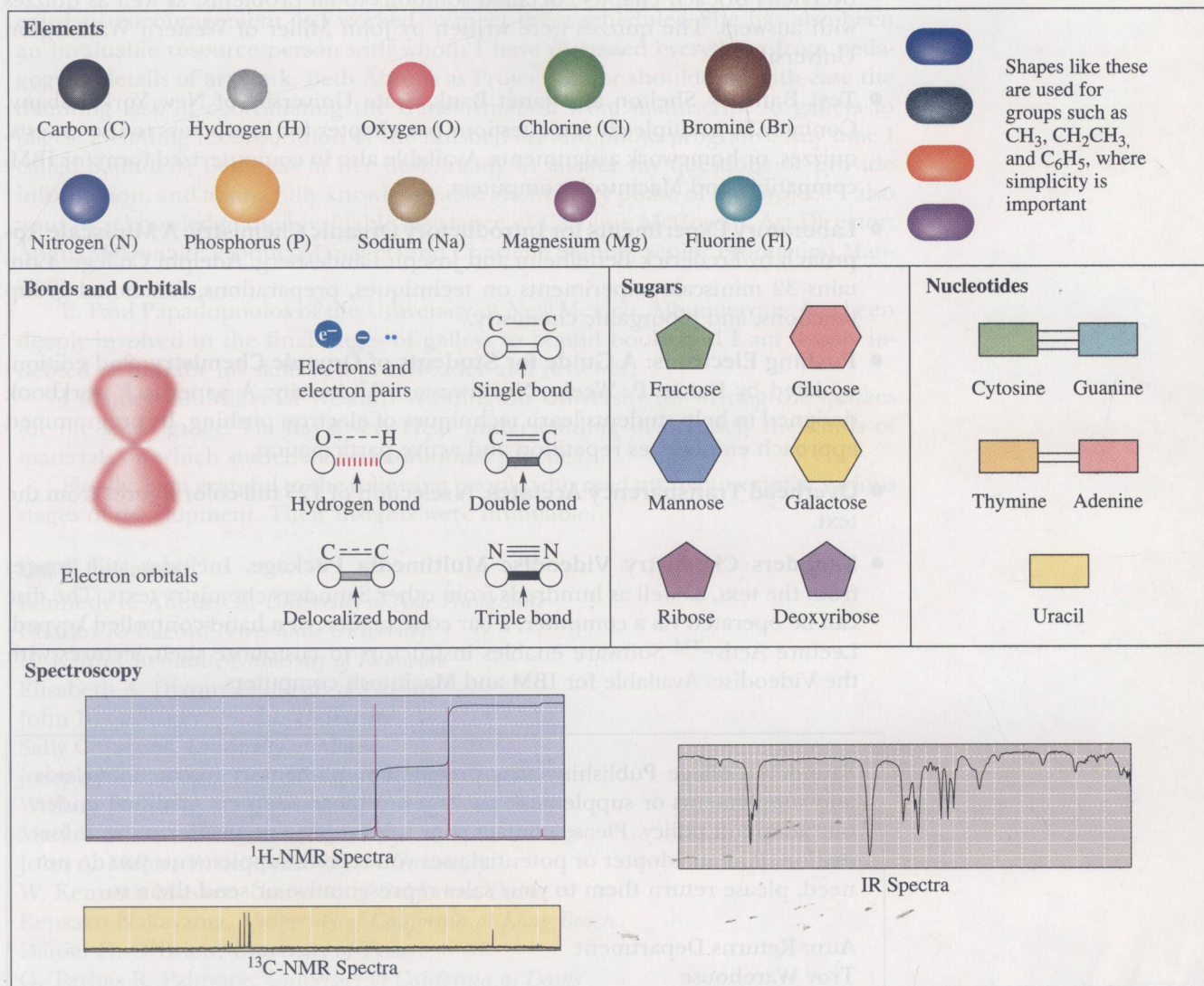
### End-of-Chapter Summaries and Summaries of Key Reactions

End-of-chapter summaries highlight all important new terms found in the chapter. In addition each new reaction is annotated and keyed to the section where it is discussed. The ends of these pages are colored for easy access.



## Color

Color is used to highlight parts of molecules and to follow the course of reactions. The graphic below shows some of the colors used consistently in the artwork in this book.



## Interviews

Four interviews with prominent scientists describe how these people became interested in chemistry as a college major, then as an educator and/or research professional. Their enthusiasm for their work is evident, and they invite students to pursue similar interests in the sciences.

## Glossary of Key Terms

Throughout the book in the margins, new terms are defined. In addition, at the end of the book is a section that gives the definitions of important terminology used in the text.

## Support Package

- **Student Study Guide and Problems Book** by Brent and Sheila Iverson of The University of Texas, Austin, and William H. Brown. Contains section-by-section overviews of each chapter, detailed solutions to all problems, as well as quizzes with answers. The quizzes were written by John Miller of Western Washington University.
- **Test Bank** by Shelton and Janet Bank, State University of New York, Albany. Contains 20 multiple-choice questions per chapter for instructors to use as tests, quizzes, or homework assignments. Available also in computerized form for IBM-compatible and Macintosh computers.
- **Laboratory Experiments for Introductory Organic Chemistry: A Miniscale Approach** by Frederick Bettelheim and Joseph Landesberg, Adelphi College. Contains 32 miniscale experiments on techniques, preparations, functional group reactions, and bioorganic chemistry.
- **Pushing Electrons: A Guide for Students of Organic Chemistry**, 2nd edition, updated by Daniel P. Weeks, Northwestern University. A paperback workbook designed to help students learn techniques of electron pushing. Its programmed approach emphasizes repetition and active participation.
- **Overhead Transparency Acetates**. A selection of 125 full-color figures from the text.
- **Saunders Chemistry Videodisc Multimedia Package**. Includes still images from the text, as well as hundreds from other Saunders chemistry texts. The disc can be operated via a computer, a bar code reader, or a hand-controlled keypad. Lecture Active™ Software enables instructors to customize their lectures with the Videodisc. Available for IBM and Macintosh computers.

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## Acknowledgments

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Finally, I am grateful to the following people who read my manuscript at various stages of development. Their insights were invaluable.

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William H. Brown  
*Beloit College, Beloit, WI*  
*July 1996*



# Periodic Table of the Elements

Periodic Table of the Elements

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Cerium	58	Praseodymium	59	Neodymium	60	Promethium	61	Samarium	62	Europium	63	Gadolinium	64	Terbium	65	Dysprosium	66	Holmium	67	Erbium	68	Thulium	69	Ytterbium	70	Lutetium	71
Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
140.115		140.9076		144.24		(144.91)		150.36		151.965		157.25		158.9253		162.50		164.9303		167.26		168.9342		173.04		174.967	

Thorium	90	Th
Potactinium	91	Pa
Uranium	92	U
Neptunium	93	Np
Plutonium	94	Pu
Americium	95	Am
Curium	96	Cm
Berkelium	97	Bk
Californium	98	Cf
Einsteinium	99	Es
Fermium	100	Fm
Mendelevium	101	Md
Nobelium	102	No
Lr	103	Lr
(262,11)	(259,10)	(258,11)

Note: Atomic masses are 1993 IUPAC values (up to four decimal places).

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