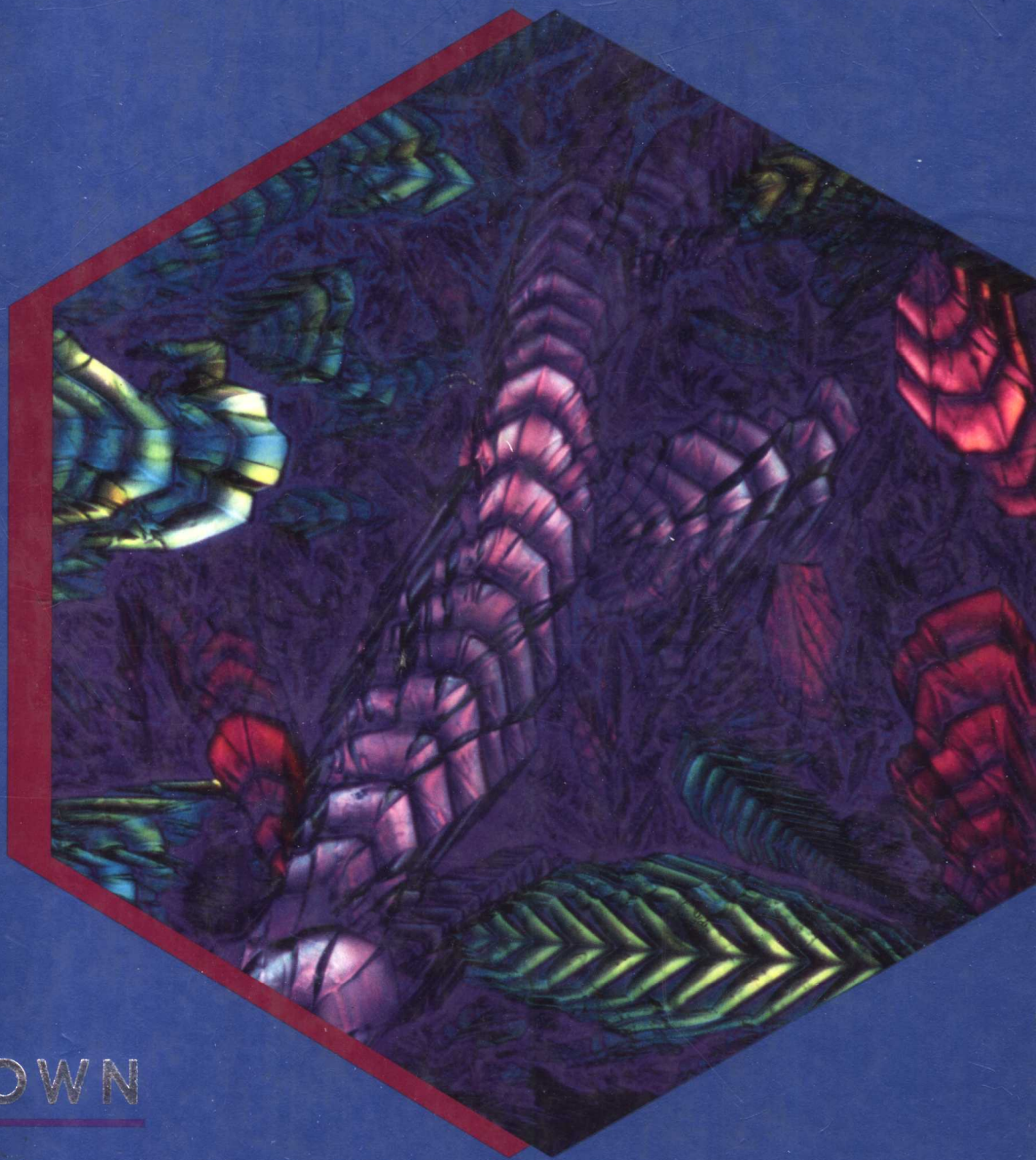


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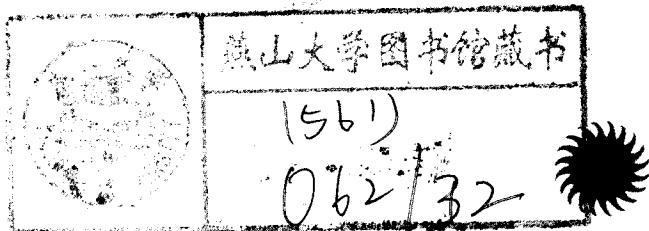


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ORGANIC CHEMISTRY

William H. Brown
Beloit College



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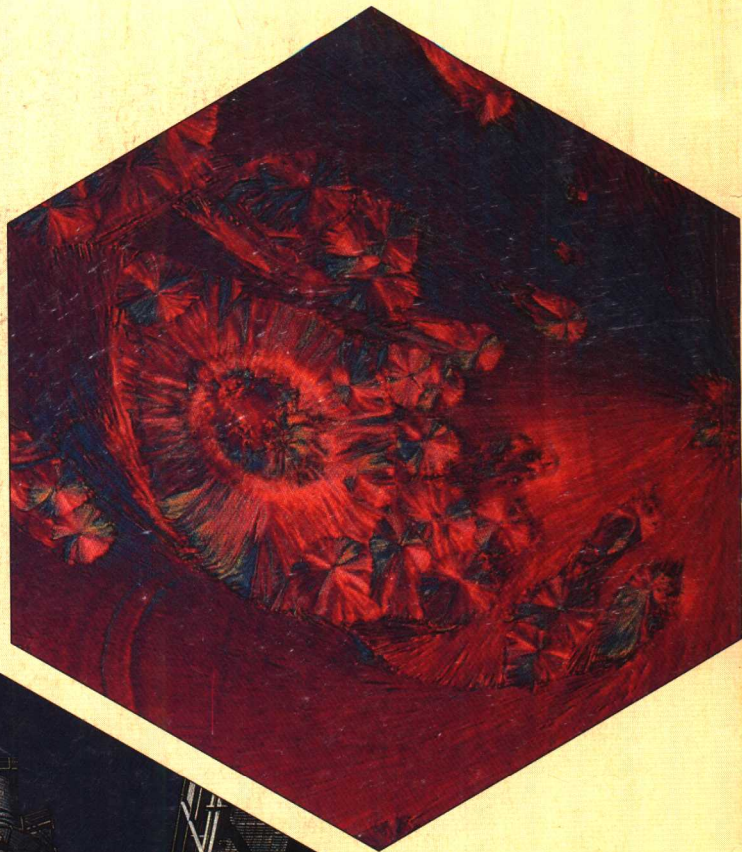
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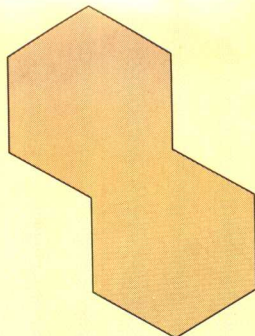
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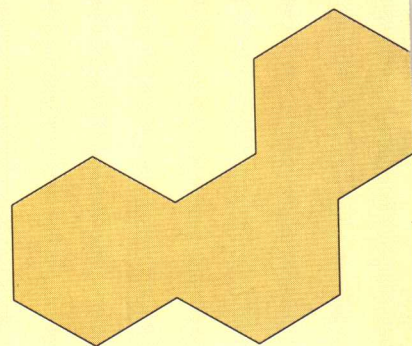
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ORGANIC CHEMISTRY



To Carolyn,
with whom
life is a joy

PREFACE

This book is intended to serve students majoring in the sciences in a one- or two-semester course in organic chemistry. I wrote the book to give students a foundation in the fundamentals of the structure of organic compounds, their reactions, and underlying reaction mechanisms. I also wish to convey to students that organic chemistry is a tool for many other disciplines, such as health and biological studies. My goal is to show students that organic compounds are all around them—in pharmaceuticals, plastics, fibers, dyes and pigments, agrochemicals, surface coatings, toiletry preparations and cosmetics, flavors and fragrances, food additives, adhesives, and elastomers. I make a special effort throughout this text to show the interrelation between organic chemistry and these areas, particularly biology, biochemistry, physiology, pharmacology, health sciences, and polymer science.

Where is the challenge in organic chemistry today? Through this text and their instructors, I hope students will see 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.

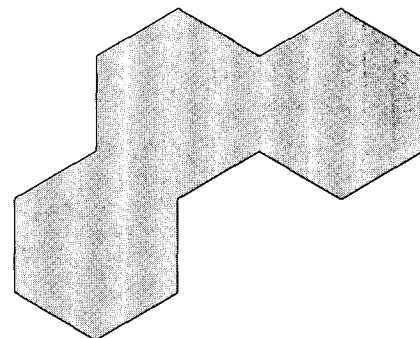
Organization

The main part of this text, consisting of Chapters 1 through 22, presents the major classes of organic functional groups in conjunction with their reactions and their reaction mechanisms. Chapters 12 through 14 within this group present the fundamentals of mass spectrometry, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$, IR, and UV-visible spectroscopy. The second part of the text, consisting of Chapters 23 through 25 is a brief introduction to the organic chemistry of three major classes of biomolecules, namely lipids, amino acids and proteins, and nucleic acids.

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 ions. It is followed by an introduction to some basic organic functional groups: alcohols, ethers, aldehydes, ketones, carboxylic acids, and esters. These particular functional groups are the ones encountered most frequently in Chapters 1 through 14. 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 moving electrons gives students two powerful tools for writing reaction mechanisms and understanding chemical reactivity. Chapter 1 concludes with an introduction to quantum mechanics and a description of covalent bonding in terms of both the valence bond model and the molecular orbital model.

Chapter 2 describes the structure and shapes of alkanes and cycloalkanes and discusses their nomenclature. 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.

Chapter 3 contains a general introduction to acid-base chemistry with emphasis on both qualitative and quantitative determination of the position of equilibrium in acid-base reactions. A knowledge of acid-base chemistry gives students another valuable tool for analyzing and understanding chemical reactivity.



Chapters 4 and 5 cover the chemistry of alkenes. Structure and physical properties are presented in Chapter 4 and then chemical reactivity in Chapter 5. Reactions are organized in the order: electrophilic additions, hydroboration, radical addition of HBr, allylic halogenation, oxidation, reduction, and polymerization. Chapter 5 concludes with a consideration of the central role of ethylene, the organic chemical industry's most important building block.

Chapters 6 and 7 continue the theme of reactivity of carbon-carbon pi bonds with the chemistry of alkynes and conjugated dienes.

Chapter 8 begins with a review of isomerism covered in earlier chapters (constitutional, conformational, *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 level of understanding of the stereochemistry of alkene addition, oxidation, and reduction reactions.

Chapter 9 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 are introduced in a preliminary way here with the reactions of alcohols with HX.

Chapter 10 presents what, in my experience, is one of the most formidable and anxiety-producing aspects of introductory organic chemistry, namely S_N1 , S_N2 , E1, and E2 mechanisms and the attendant concepts of stereochemistry, kinetics, and relationships between structure and chemical reactivity. As I tell students, the difficulty does not lie in any single part of this material; no part of it is any more difficult than material already covered. The difficulty, rather, is in the number of concepts to be assimilated at one time. "Now," I tell students, "you will have to sing, dance, chew gum, snap your fingers, and whistle all at the same time." It is for these reasons that I present nucleophilic substitution after the chemistry of alkenes and alkynes, conjugated dienes, chirality, and alcohols. 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 β -elimination then become a vehicle for integration of previously covered chemistry into a larger pattern.

Chapter 11 is a logical extension of nucleophilic substitutions as applied to the synthesis of ethers and the reactions of epoxides.

Chapters 12 through 14 examine several instrumental methods for analyzing molecular structure and relate these methods to functional groups that have been studied to this point. First is mass spectrometry (Chapter 12), the instrumental technique by which molecular formulas are determined. Given the placing of this chapter, students are prepared to study the mass spectrometry of alkanes, alkenes, alkynes, alcohols, ethers, and epoxides. The mass spectrometry of other classes of organic compounds is presented in subsequent chapters. Chapter 13 presents the fundamentals of both $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy, while IR and UV-visible spectroscopy are covered in Chapter 14. While this material is presented as a cluster of chapters midway through the text, the chapters are free-standing and can be used in other orders as appropriate to a particular course.

Chapters 15 and 16 present the chemistry of aromatic compounds. The first of these chapters concentrates on structure and nomenclature of aromatic compounds, the concept of aromaticity, and the structure and acid-base properties of phenols. The second of these chapters is devoted to aromatic substitution reactions.

Chapters 17 through 21 concentrate on the chemistry of carbonyl-containing compounds. First is the chemistry of aldehydes and ketones in Chapter 17. Immediately following is the chemistry of carbohydrates in Chapter 18. The reason for this placement is that the chemistry of carbohydrates is built on the chemistry of two functional groups, namely aldehyde and ketone carbonyl groups and alcohol hydroxyl groups.

Chapters 19 and 20 present the chemistry of carboxylic acids and their functional derivatives. Following in Chapter 21 is the chemistry of enolate anions, including the acetoacetic ester and malonic ester syntheses and the Michael reaction.

Chapter 22 completes the introduction to organic functional groups with a presentation of the chemistry of aliphatic and aromatic amines.

Finally, in Chapters 23 through 25, the organic chemistry of lipids, amino acids and proteins, and nucleic acids are presented. Chapter 23 covers the structure of the major classes of lipids: triacylglycerols, fatty acids and prostaglandins, steroids, phospholipids, and the fat-soluble vitamins. Chapter 24 gives considerable attention to the acid-base properties of amino acids and then continues with an introduction to primary, secondary, and tertiary structure of polypeptides. The stereopairs of ribonuclease, hemoglobin, and myoglobin are particularly dramatic and valuable as teaching tools. The concentration in Chapter 25 is on primary, secondary and tertiary structure of DNA and solid-phase synthesis of DNA. An interesting "Chemistry in Action" box discusses the organic compounds used in the treatment of neoplastic diseases.

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 250 pieces of art—many never seen before in organic texts—by professional artists John and Bette Woolsey.

Stereopairs

A collection of over 50 stereopairs have been prepared for this text, each chosen to reinforce the concept of organic chemistry as a three-dimensional science. Student reaction to these stereopairs ranges from "cool" to "spectacular." Each copy of the text is equipped with a pair of stereoglasses for easy viewing. Stereoart is indicated by the following icon:



Chemistry in Action Boxes

These boxes illustrate applications of organic chemistry to everyday settings. Topics range from Drugs that Lower Plasma Levels of Cholesterol, to Carbamate Insecticides, and Chirality and the Search for Extraterrestrial Life.

In-Chapter Examples

There are an abundance of in-chapter examples. Solutions are given in detail so that students can follow the logic behind each step. Following each in-chapter example is a comparable in-chapter problem designed to give students the opportunity to practice solving related problems.

End-of-Chapter Summaries

End-of-chapter summaries highlight all key reactions found in a chapter. Each reaction is annotated and keyed to the section where it is discussed. For those chapters with no new reactions, for example the chapters on spectroscopy and chirality, prose summaries are given.

End-of-Chapter Problems

There are plentiful end-of-chapter problems—more than typically given in organic texts. All problems are categorized by topic. A tetrahedral icon (Δ) is used next to applied problems. A blue number indicates that a problem is more challenging.

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.

Color

Color is used to highlight parts of molecules and to follow the course of reactions. The graphic on the next page 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.

































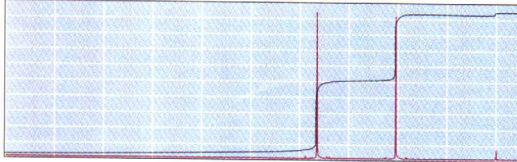
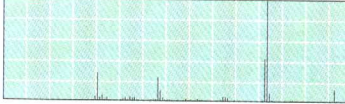
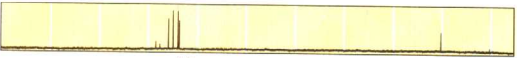
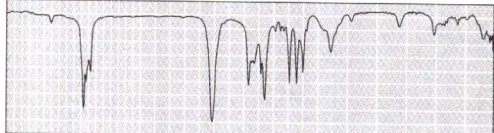
Bio-organic Chemistry

Bio-organic chemistry is emphasized throughout. An invaluable reference for health-related organic chemistry is Goodman and Gilman's *The Pharmacological Basis of Therapeutics*, 8th Edition, A. Goodman Gilman, T. W. Rall, A. S. Nies, and P. Taylor, Editors, (Pergamon Press, New York, 1990).

Glossary of Key Terms

At the end of the book is a section that gives the definitions of important terminology used in this text.

COLOR KEY

Elements					
					   
Carbon (C)	Hydrogen (H)	Oxygen (O)	Chlorine (Cl)	Bromine (Br)	
					
Nitrogen (N)	Phosphorus (P)	Sodium (Na)	Magnesium (Mg)	Fluorine (F)	
Bonds and Orbitals			Sugars		Nucleotides
Positive					
	Electrons and electron pairs	Single bond	Fructose	Glucose	
Negative					
Electron orbitals	Hydrogen bond	Double bond	Mannose	Galactose	
					
	Delocalized bond	Triple bond	Ribose	Deoxyribose	Uracil
Spectroscopy					
					
¹ H-NMR Spectra			Mass Spectra		
					
¹³ C-NMR Spectra			IR spectra		

Support Package

- Student Study Guide and Problems Book by Brent and Shiela Iverson of the University of Texas, Austin. Contains section-by-section overviews of each chapter and detailed solutions to all text problems. Each reaction chapter includes a "reactions grid," which organizes in a unique way the transformations of each new functional group and the reagent(s) required to bring about each transformation.
- 1001 Ways to Pass Organic Chemistry: A Guide for Helping Students Prepare for Exams by Shelton and Janet Bank, State University of New York, Albany. Contains 1001 problems with answers and tips for problem solving.

- Test Bank by Shelton and Janet Bank, State University of New York, Albany. Contains 25 multiple-choice questions per chapter for instructors to use for tests, quizzes, or homework assignments. Available also in computerized form for IBM-compatible and Macintosh computers.
- Pushing Electrons: A Guide for Students of Organic Chemistry, 2/e (Updated Edition) 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.
- Organic Polymer Chemistry: A Primer by Bruce M. Novak, Polymer Science and Engineering Department, University of Massachusetts. A supplemental chapter in paperback containing an introduction to polymer chemistry: molecular weight distributions, polymer morphology, step-growth and chain polymerizations, ring-opening metathesis polymerizations, and conjugated polymers through ROMP techniques. Also included are a chapter summary, end-of-chapter problems, and three "Chemistry in Action" boxes.
- Overhead Transparency Acetates. A selection of 125 full-color figures from the text.
- Saunders Chemistry of Life Videodisc Multimedia Package. Includes still images from this 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.
- Chemoffice Ltd. 2.0 (Chem Draw and Chem 3D) is a software package from Cambridge Scientific that provides students with the capabilities to draw molecular structures, and to manipulate them in three-dimension. A User's Guide and Quick Reference Card, written exclusively for Saunders College Publishing, accompany the software.

The following Organic Chemistry Laboratory Manuals published by Saunders College Publishing can be used along with this text:

- Introduction to Organic Laboratory Techniques, A Microscale Approach, 2/e by Pavia, Lampman, Kriz, and Engel.
- Introduction to Organic Laboratory Techniques, 3/e by Pavia, Lampman, and Kriz.
- Organic Chemistry Laboratory: Standard and Microscale Experiments by Rodig, Bell, and Clark.
- Experimental Organic Chemistry: A Miniscale Approach by Roberts, Gilbert, and Martin.

Acknowledgments

While one or a few persons are listed as “author” of any textbook, the book is in fact the product of collaboration of many individuals, some obvious, others not so obvious. It is with gratitude that I herein acknowledge the contributions of the many. It is only fitting to begin with John Vondeling, Vice President and Publisher of Saunders College Publishing. John’s contribution began with the faith that I could do this book and then marshalling the support systems necessary to bring it from rough manuscript to bound book form, assembling the elements of the supplemental materials, and finally bringing to bear his keen sense of the marketplace.

Sandi Kiselica has been a rock of support as Developmental Editor. I so appreciate her ability to set challenging but manageable schedules for me and then her constant encouragement as I worked to meet those deadlines. She was also an invaluable resource person with whom I could discuss everything from pedagogy to details of art work.

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J. William Suggs of Brown University has provided a unique contribution, the majority of Chemistry in Action boxes. Bill has both industrial and academic background and brings an unusually broad range of professional experience to the writing of these informative pieces.

I also want to acknowledge other colleagues who contributed their comments and suggestions to this book.

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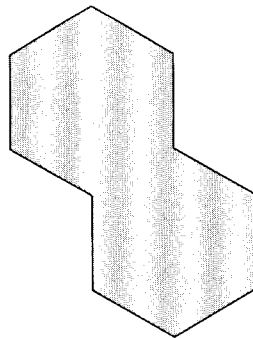
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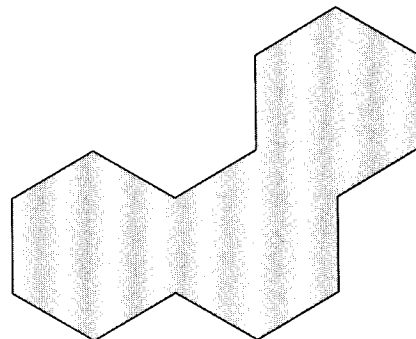
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Darrell J. Woodman, *University of Washington*
Ali Zand, graduate student, *Michigan State University*

I have enjoyed writing this text, and I hope that instructors and students alike find in it a measure of the excitement I feel for organic chemistry.

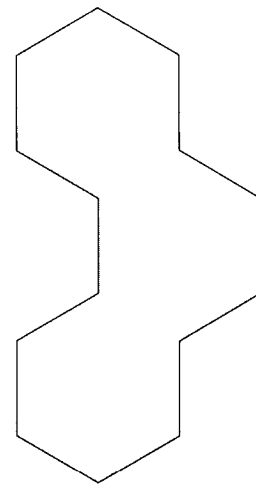
William H. Brown
Beloit College
Beloit, WI
July 1994



ORGANIC CHEMISTRY



GLOSSARY



Acetal A functional group consisting of a carbon bearing a combination of two —OR or —OAr groups. Acetals are stable to nucleophilic reagents and aqueous base but undergo hydrolysis in aqueous acid to form the carbonyl group of an aldehyde or ketone and two —OH groups. Acetals are often used as a protecting group for the carbonyl groups of aldehydes and ketones or the —OH groups of a glycol.

Achiral An object that lacks chirality.

Activating group A group on a benzene ring that causes the rate of an electrophilic aromatic substitution to be faster than that for benzene.

Acyl group The characteristic feature of an acyl group is RCO— or ArCO—.

Acylation A reaction involving substitution of an acyl group (RCO— or ArCO—) for a hydrogen atom. Examples of acylation reactions are Friedel-Crafts acylation to form an aryl ketone, conversion of an alcohol to an ester, and conversion of an amine to an amide.

Addition polymerization A type of polymerization in which monomer units are joined together without loss of atoms.

Aliphatic compound A term used to refer to nonaromatic hydrocarbons (alkanes, alkenes, alkynes) and their derivatives.

Alkylation A reaction involving substitution of an alkyl group for a hydrogen atom. Examples of alkylation reactions are Friedel-Crafts alkylation of aromatic rings, alkylation of enolate anions, and Williamson ether synthesis.

Allylic A term used to refer to a position next to a carbon-carbon double bond. The carbon atom next to a carbon-carbon double bond is an allylic carbon, and a substituent on an allylic carbon is an allylic substituent. 3-Bromocyclohexene, for example, is an allylic bromide.

Angle strain Strain in a molecule or ion arising from the creation of either abnormally large or abnormally small bond angles.

Angstrom, Å A unit of length. $1 \text{ Å} = 10^{-10} \text{ m}$.

- Annulene** A cyclic hydrocarbon with continuous alternation of single and double bonds. Examples of aromatic annulenes are [14]annulene and [18]annulene.
- Anomeric carbon** The new stereocenter formed in a monosaccharide as a result of cyclic hemiacetal formation. The resulting diastereomers are given the special name anomers.
- Anti addition** Addition of atoms or groups of atoms from opposite sides or faces of a pi bond. In cyclic systems, anti addition is equivalent to *trans* coplanar addition.
- Antiaromatic compound** According to Hückel's criteria, a compound that is cyclic, planar, has continuous overlap of $2p$ orbitals, and contains $4n$ pi electrons. An antiaromatic compound is less stable than its acyclic analog of the same number of pi electrons. Cyclobutadiene, for example, is antiaromatic.
- Antibonding MO** A molecular orbital where the electron density is concentrated outside the region between the two nuclei and consequently there is little or no electron density between nuclei to offset nuclear repulsion. An antibonding MO is higher in energy than the atomic orbitals from which it is formed.
- Aprotic solvent** A solvent that cannot serve as a hydrogen bond donor; nowhere in the molecule is there a hydrogen bonded to an atom of high electronegativity so as to provide a dipole with hydrogen bearing the partial positive charge.
- Arene** An aromatic hydrocarbon. Benzene is the simplest arene.
- Aromaticity** (see Hückel's criteria for aromaticity)
- Asymmetric carbon** A term used, when chirality in organic molecules was first recognized, for a tetrahedral carbon atom with four different groups attached to it.
- Aufbau principle** A rule stating that orbitals in atoms and molecules fill in order of increasing energy from lowest to highest.
- Axial bonds** Bonds parallel to the axis of the imaginary sphere in which a chair conformation of a cyclohexane ring is centered. Three axial bonds (those on carbons slightly above the equator) point upward; the other three axial bonds (those on carbons slightly below the equator) point downward.
- Base peak** The most abundant ion current recorded in the detector of a mass spectrometer; the tallest peak in the mass spectrum. The relative abundances of all other peaks in a mass spectrum are reported as percentages of abundance of the base peak.
- Basicity** An equilibrium property measured by the position of equilibrium in an acid-base reaction.
- Benzylic** A term referring to a carbon atom bonded to a benzene ring. An anion, radical, or cation derived from a benzylic carbon is referred to as a benzylic anion, radical, or cation.
- Betaine** A neutral substance with nonadjacent negative and positive charges. Examples are the first intermediate in a Wittig reaction and the zwitterion form of an α -amino acid.
- Bimolecular reaction** A reaction in which two reactants undergo a chemical change in the transition state of the rate-determining step.
- Bond dissociation energy** The energy required to break a chemical bond in such a way that one electron from each bonding pair remains with each atom; that is, the bond is broken homolytically.
- Bond order** One-half the difference of the number of electrons in bonding molecular orbitals minus the number in antibonding molecular orbitals.
- Bonding MO** A molecular orbital where the electron density is concentrated in the region between the two positively charged nuclei and serves to offset the repulsive interaction between them. A bonding MO is lower in energy than the atomic orbitals from which it is formed.
- Brønsted acid** A proton donor.
- Brønsted base** A proton acceptor.
- Chain initiation** A step in polymerization. The characteristic feature of a chain initiation step is formation of a reactive intermediate (a radical, an anion, or a cation) from less reactive compounds.
- Chain length** The number of times that a cycle of chain propagation steps repeats in polymerization.
- Chain propagation** A step in polymerization. The characteristic feature of a chain propagation step is reaction of a reactive intermediate (a radical, an anion, or a cation) and a molecule to give a new reactive intermediate or two compounds, one a new molecule and the other a new reactive intermediate.
- Chain reaction** A reaction that, once initiated, continues by repetition of a set of chain propagation steps. Chain propagation steps are the product-forming steps of a chain reaction.
- Chain termination** A step in polymerization. The characteristic feature of a chain termination step is destruction of reactive intermediates.
- Chair conformation** A puckered conformation of a cyclo-