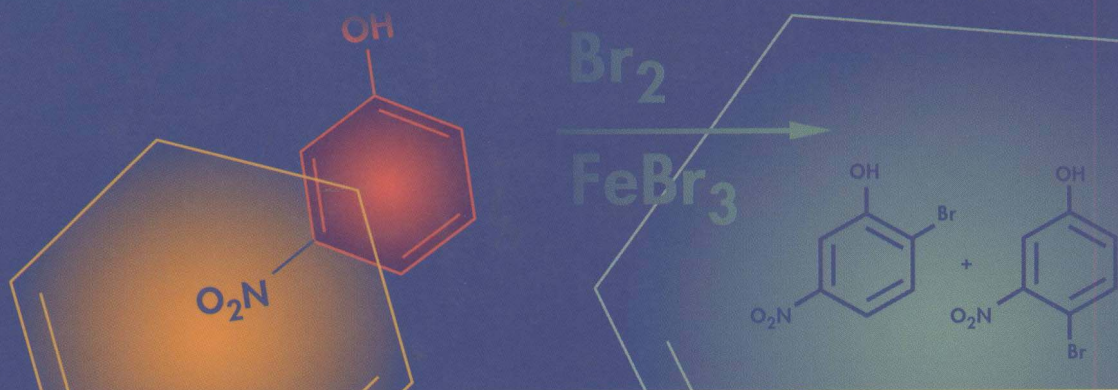


COLUMBIA REVIEW

# HIGH YIELD<sup>TM</sup>

## Organic Chemistry

by STEPHEN BRESNICK, M.D.



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# COLUMBIA REVIEW

**HIGH-YIELD ORGANIC CHEMISTRY**

**Stephen D. Bresnick, M.D.**

President and Director  
Columbia Review, Inc.  
San Francisco, California



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# **COLUMBIA REVIEW**

**HIGH-YIELD ORGANIC CHEMISTRY**

# Preface

preface

*High-Yield Organic Chemistry* is an easy-to-read, efficient, and high-quality review book for first-year, college-level organic chemistry. The book focuses on a conceptual review of core organic chemistry topics and for its size covers an amazing amount of material. For mastery of review material, over 340 practice questions with solutions are provided. The book is designed for all college students or others wishing to understand and review the major concepts of organic chemistry. Students who are pre-health, chemistry, or non-science majors will benefit from this book.

*High-Yield Organic Chemistry* is one of four books in the *High-Yield Undergraduate Science Review Series* by Williams & Wilkins. The series also contains *High-Yield General Chemistry*, *High-Yield Physics*, and *High-Yield Biology*. This series has been designed to make these four important college sciences easier to understand and master. All the High-Yield books contain a science review, many examples and sample problems, and several hundred practice questions with answers and explanations.

The author of this series, Dr. Stephen Bresnick, is an expert in helping students understand, review, and retain basic college science material. Dr. Bresnick understands that many students work their way through college courses without really comprehending the material they are supposed to be learning. He has designed these four books to help students **understand science better and improve their course grades**. In addition, the series has been designed to help students prepare for **post-graduate and pre-professional tests**, such as the GRE, MCAT, DAT, PCAT, VET, OAT, and other tests. Dr. Bresnick is a physician and educator who both teaches and writes science review material for college students. He is currently Director of **Columbia Review**, a national test-preparation company specializing in science and English review for pre-medical school students.

## Organization

There are three sections in this book. Each section corresponds to the specific topics that most college students study in organic chemistry courses. The topic review emphasizes conceptual learning and provides numerous sample problems and examples. Each section of the book is followed by several sets of review questions and their solutions.



# Acknowledgments



The author wishes to thank Dr. William Bresnick and Dr. Nori Kawahata for their contributions. In addition, many thanks to the staff of Williams & Wilkins for their dedication in creating a great high-yield review book for organic chemistry. I especially wish to thank Lee Elkins, Danielle Santucci, Elizabeth Nieginski, Jane Velker, Tim Satterfield, and Kevin Thibodeau for their expertise and assistance with this important project.

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# I

## SECTION

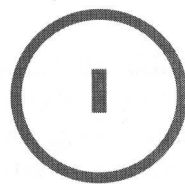
### General Concepts and Hydrocarbon Chemistry

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## I. Basic Introduction

**Success in organic chemistry requires a thorough knowledge and understanding of the basics.** These review notes show an assortment of reactions that give a general overview of organic chemistry. **Do not just memorize reactions!** Instead, familiarize yourself with how and why the reactions occur. Use the principles and concepts presented in the Organic Chemistry Review Notes and subsequent practice to gain an understanding of the types of processes that molecules undergo as they try to attain more favorable energy states. The key is to understand trends and principles.

The appendix to the Organic Chemistry Review Notes provides a summary of the rules for nomenclature in organic chemistry. As you review each functional group, be sure to flip back to this appendix to review the nomenclature for that group.

So what are the basics?

1. Atoms are mostly fluffy electron clouds (atomic orbitals). What differentiates them is the number of electrons in the outer shell and how far away this shell is from the nucleus. These outer shell electrons determine physical properties and reactivity.
2. Molecules are formed when two atoms join their atomic orbitals to form a larger electron cloud [molecular orbital (MO)]. The sharing of electrons in an MO constitutes a covalent bond. Electrons can move within an MO and they gather around the more electronegative atom of the bond. This focus of electrons in particular regions of a molecule affects the physical properties and chemical reactivities of the molecules.
3. In most cases, bonds form between species that are electron deficient (**electrophiles**) and those that are electron rich (**nucleophiles**). Thus, it is important to be able to recognize which types of atoms and molecules are nucleophiles and which are electrophiles.
4. When analyzing chemical reactions, remember that a reaction is a collision between two molecules. Organic reactions (i.e., bonds breaking and forming) occur because they involve energy-releasing processes or because enough energy is applied to force the reaction. In general, everything strives toward lower energy.
5. Lower-energy species are more stable and less reactive, whereas higher-energy species are less stable and more reactive.

## II. Electronegativity and Bond Formation

### A. IMPORTANCE OF ELECTRONEGATIVITY AND VALENCE ELECTRONS IN BOND FORMATION

A great way to remember the electronegativity order of key elements, going from the highest electronegativity to the lowest, is to learn the expression, **FONClBrISCH** (pronounced “fawn-



cul-brish"). This expression will help you to remember that the key elements (fluorine, oxygen, nitrogen, chlorine, bromine, iodine, sulfur, carbon, and hydrogen) descend predictably in electronegativity strength compared to one another. **Electronegativity is defined as the ability of an atom to attract electrons.**

From this order, recognize that **electronegativity increases as you move to the right on the periodic table.** Halogens (group VII), with seven valence electrons, need only one more electron to attain the energetically favorable complete outer-shell octet. Thus, they have a relatively high affinity for electrons. After gaining one electron, group VI elements still need another electron to reach a complete octet; thus, their affinity for an electron is not as great as that of the halogens. Group V atoms have an even lower affinity for an electron.

**Electronegativity decreases as you move down the periodic table.** Concurrently, the atomic radii of the elements increase greatly. An electron added to the outer shell of a relatively large atom such as iodine does not feel as strong a nuclear charge (because of **shielding** by the electrons in energy levels below) as an electron added to fluorine. Also, the outer-shell electrons of a large atom such as iodine are not held as tightly as those of smaller atoms because of their greater distance from the positively charged nucleus.

**As you move to the left on the periodic table,** the elements are increasingly willing to give up electrons. By releasing a few electron(s), the next lower energy level that contains a full octet becomes the shell. For example, in group IA,  $\text{Na}^+$  is Na that has given up one electron to expose a full outer shell of electrons.

**All atoms not in this list have electronegativities lower than hydrogen.** All members of F O N C l B r I S C H (except H) are on the right side of the periodic table. They need to gain three or fewer electrons to obtain a complete octet of electrons in their outer shell.

**The number of valence electrons determines how many bonds are formed.** Halogens (group VII) have seven electrons in their outer shell and generally form one bond to establish a complete octet. Atoms in group VI (oxygen) have six valence electrons, so they generally form two bonds to complete an octet. Nitrogen and other group V elements form three bonds to complete their octet. Carbon, one column to the left on the periodic table, has four valence electrons and forms four bonds.

## B. TYPES OF BONDS

### 1. IONIC BONDS

**Ionic bonds occur between two atoms of different electronegativities.** The electronegative atom takes an electron from another atom that possesses a low ionization potential (willing to give up an electron to obtain a completely filled outer shell of electrons).

Typical ionic bonds involve halogens and metals (e.g., NaCl, KI). **These bonds are strong.** Furthermore, crystal lattices form, involving a highly ordered system with extensive intermolecular bonding. The intermolecular bonds give these compounds high melting and boiling points. To solvate these molecules, the intermolecular interactions of the solid must be replaced by interactions with the solvent. In other words, polar solvents must be used to solvate these highly polar molecules. Ionic bonds also occur between charged clusters of atoms ( $\text{NH}_4^+\text{OH}^-$ ,  $\text{NH}_4^+\text{CH}_3\text{COO}^-$ ).

### 2. COVALENT BONDS

**Covalent bonds involve the sharing of electrons, but it is not a "give-and-take" relationship as with ionic bonds.** They occur in diatomic molecules, such as  $\text{O}_2$  or  $\text{Cl}_2$ , and between atoms with similar electronegativities. **Polar covalent bonds** involve atoms that have different

electronegative strengths, but not to the point where an ionic bond forms. The movement of electrons toward the more electronegative atom results in a partial positive charge on one end of the bond (lower electronegativity end) and a partial negative charge on the other end (higher electronegative end).

### 3. HYDROGEN BONDS (H-BONDS)

**Hydrogen bonds are relatively weak intermolecular interactions in which a slightly acidic (partially + or  $\delta^+$ ) hydrogen forms a weak dipole interaction with a neighboring basic (partially - or  $\delta^-$ ) atom.** Look for hydrogen atoms attached to N, O, and F. These atoms tend to be good donors of hydrogen toward H-bonds. Good acceptors are electronegative atoms with lone pair electrons, such as O, N, and F. Hydrogen bonds account for many physical properties of compounds in organic chemistry.

## C. ATOMIC, MOLECULAR, AND HYBRID ORBITALS

### 1. GENERAL IDEAS

The **atomic orbitals (AO)** are theoretic regions around the nucleus where the probability of finding an electron is high. Each energy level contains its own AO.

The **covalent bond** involves a sharing of electrons. **This bond between two atoms is an overlap of two atomic orbitals.** The overlap of two AO forms two MO—one bonding MO (lower energy) and one antibonding MO (higher energy). Electrons fill the lower-energy bonding MO first, and then they fill the higher-energy antibonding MO. If the number of electrons in the bonding orbitals is the same as that in the antibonding orbitals, no bond will form between the two atoms.

The **hybridization** of AO involves a mixing of AO on an atom to create a hybrid AO. These new AO allow for greater overlap when forming MO, leading to a stronger (lower-energy) bond. The hybridization determines the shape of the molecule.

### 2. ATOMIC ORBITALS

Atomic orbitals describe a cloud in which electrons of a particular energy level are likely to be found about the nucleus of an atom. These orbitals have specific shapes, depending on their energy.

For organic chemistry, it is important to know the following:

**s orbital:** Spherically symmetric about the nucleus

**p orbital:** Dumbbell shaped with nucleus at the center

With the exception of the first energy level, which contains only the s orbital, each principal energy level has one s orbital and three p orbitals arranged  $90^\circ$  from each other (Figure 1-1).

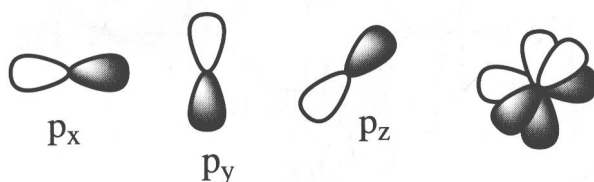


Figure 1-1. The arrangement of the p orbitals.

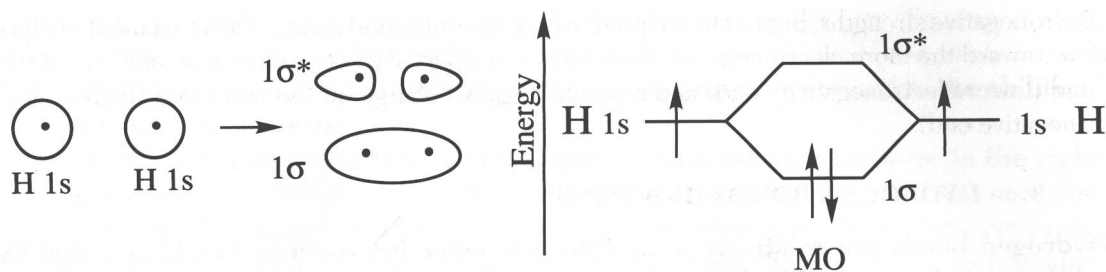


Figure 1-2. Molecular orbital diagram for  $\text{H}_2$ .

Each orbital can hold two electrons. Remember that the filling order is  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^6$ ,  $4s^2$ ,  $3d^{10}$ ,  $4p^6$ ,  $5s^2$ ,  $5p^6$ , and so on, filled from lowest to highest energy.

### 3. MOLECULAR ORBITALS

Molecular orbitals, one bonding and the other antibonding, are created when atomic orbitals from two atoms combine and form a single electron cloud. The two electrons in this MO are shared by the contributing atoms. Each MO can hold two electrons. Two simple examples follow.

#### Example 1-1: $\text{H}_2$ (Figure 1-2)

- Two  $1s$  orbitals combine to form  $1\sigma$  (bonding) and  $1\sigma^*$  (antibonding) MO.
- $\sigma$  represents an MO formed from a direct **end-to-end overlap of AO**.
- $\sigma^*$  represents a molecular orbital with **no atomic orbital overlap**.
- Two electrons (one from each H) fill the  $1\sigma$  MO, and a bond forms.

#### Example 1-2: $\text{He}_2$ (Figure 1-3)

- Four electrons (two from each He) fill the  $1\sigma$  and  $1\sigma^*$  MO.
- Because both the higher-energy  $1\sigma^*$  MO and the  $1\sigma$  MO are occupied, a bond does not form between two He atoms. This type of orbital filling occurs for all noble gases and is the reason why they do not exist as diatomic species. It is energetically preferable for electrons to remain in the lower-energy AO. A bond will form only when electrons fill more “bonding” MO than antibonding MO.

This diagrammatic method is an easy way to conceptualize simple molecules. Such diagrams become exponentially more difficult as more electrons and atoms are added to the picture, but they give you an idea of what to think about as you draw a line on paper to designate a bond.

Remember that bonds form because it is energetically more favorable for the atoms to be bonded rather than unbound. In Figures 1-2 and 1-3, note that the energy of the  $1\sigma$  MO is lower

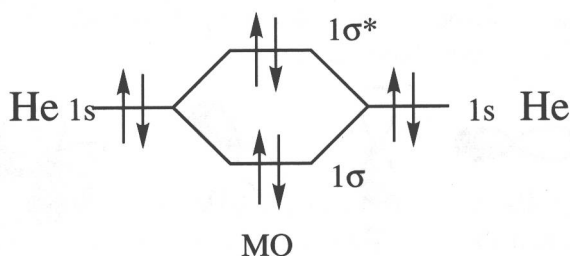


Figure 1-3. Molecular orbital diagram for  $\text{He}_2$ .