

# ORGANIC CHEMISTRY

concepts and applications

James O. Schreck



# **ORGANIC CHEMISTRY**

## **concepts and applications**

**James O. Schreck**

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF NORTHERN COLORADO  
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with 93 illustrations

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## Preface

This textbook is written with a functional group approach and incorporates a mechanistic viewpoint to explain the reactions of organic compounds. Written for a one-semester or two-quarter course, it is intended for nonmajors in the paramedical curriculum, home economics, nursing, and industrial arts, and for other nonscience majors who want or need to take a course in introductory organic chemistry.

This book treats the International Union of Pure and Applied Chemistry and common systems of nomenclature for a particular functional group, the common laboratory preparations of that group, and the characteristic class reactions. Mechanisms are used throughout. Energy considerations and profiles are included to illustrate a mechanism. Practical organic chemistry is stressed where appropriate. Some applications include discussions on insect pheromones, analysis of alcoholic beverages, the use and misuse of drugs, commercial materials derived from benzene, food additives, a stereospecific world, and the free radical theory of human aging. Chapter 14 is an important application of organic chemistry; in fact, it is a discussion of the organic chemistry of the living system. In addition, the fourteen chapters include a review of fundamental concepts, aliphatic and aromatic hydrocarbons, stereochemistry, organic halides, alcohols and phenols, ethers and epoxides, aldehydes and ketones, carboxylic acids and their derivatives, organic nitrogen compounds, structure determination through the use of classical and spectral methods, and biomolecules.

Each chapter consists of core material, a summary of the important concepts, a list of important terms for the student's vocabulary of organic chemistry, and a set of problems and questions that review the concepts presented in the chapter. Furthermore, several parts of these problems and questions are answered or explained so that students can check their progress. The answers to all the questions within the chapter are given in the back of the text; the answers to the questions at the end of the chapter are in the instructor's manual. Finally, a self-test is provided at the end of each chapter containing material that I consider of most importance.

Chapter 1 introduces the student to the functional groups that will be encountered throughout the text. After a discussion on the distinction between ionic and covalent bonding, the student is introduced to the concept of the hybridized carbon atom and the energy requirements of organic reactions.

Instead of using the traditional approach of teaching the chemistry of alkanes, alkenes, and alkynes in three separate chapters, I have combined the chemistry of aliphatic hydrocarbons in two chapters. Chapter 2 deals with the structure, nomenclature, and laboratory preparations of the aliphatic hydrocarbons. The concept of the hybridized carbon atom for alkanes, alkenes, and alkynes is reviewed first. The nomenclature of alkanes is presented in detail and the nomenclature of alkenes and alkynes builds upon the IUPAC rules for alkanes. Although methods are available, none are presented for the laboratory synthesis of alkanes. Instead a discussion of petroleum as a source of alkanes is given. The laboratory methods for preparing alkenes are illustrated by dehydrohalogenation and dehydration. Mechanisms are discussed for each method and the presence of carbonium ions in the biochemical synthesis of cholesterol is illustrated. For alkynes, dehydrohalogenation and the reaction of sodium acetylides with primary alkyl halides are presented as methods of forming alkynes. Other applications found in this chapter are geometrical isomers among insect pheromones and the relationship of the carbon-carbon triple bond to the birth control pill. Chapter 3, on the other hand, considers the reactions of aliphatic hydrocarbons. For alkanes, the reactions discussed are free radical substitution (predominantly for methane and propane) and combustion. Also discussed are combustion of alkanes with respect to gasoline and pollution; the typical reactions of alkenes dealing with electrophilic addition, polymerization and polymers as an application of free radical addition in alkenes; and tautomerization and acidity of alkynes.

Chapter 4 deals with the chemistry of aromatic hydrocarbons, particularly benzene. The structure, molecular orbital picture, and nomenclature of benzene and its derivatives are presented. These concepts are then followed by a discussion of electrophilic aromatic substitution. The concept of resonance is used to explain orientation of substitution in benzene derivatives but can be omitted in a one-quarter course. The students are taught how to synthesize using the orientation concept. The chemistry of some other benzene derivatives (for example, naphthalene) and the free radical substitution in arenes is included but usually omitted in the short course. The chapter concludes with a discussion of some commercially important products derived from benzene.

The outline of Chapter 5, on isomerism, is not traditional and is the result of an idea developed by Dr. Gordon Tomasi and myself. Its purpose is to present in a uniform manner the most important concepts of isomerism and usage of terminology, particularly since the organic student of one quarter is the biochemistry student of the next quarter at our university.

Chapters 6 through 11 are concerned with the chemistry of the functional

groups. Each chapter is written in basically the same manner: structure, nomenclature, laboratory methods, of synthesizing, reactions involved, and uses or occurrences of compounds containing the functional group.

In Chapter 6 the laboratory methods discussed for introducing a hydroxy group into a molecule include hydrolysis of alkyl halides, Grignard synthesis, and hydroboration-oxidation. The reactions of alcohols and phenols include the formation of alkyl halides (alcohols), dehydration (alcohols), acidity (alcohols and phenols), ester formation (alcohols and phenols), oxidation (alcohols), and electrophilic aromatic substitution (phenols). The reaction dealing with oxidation of alcohols contains a discussion of the roadside breath test. The chapter concludes with an introduction to gas chromatography and its use in the analysis of alcoholic beverages.

Chapter 7 deals with the four types of reactions that an alkyl halide can undergo:  $S_N1$ ,  $S_N2$ ,  $E1$ , and  $E2$ . A section on organochlorine insecticides is included. Topics that are included in the text but are of less importance and not covered in a short course include carbene and benzyne formation and nucleophilic and electrophilic substitution reactions of aromatic halides.

The applications in Chapter 8 are the uses of ethers and products derived from epoxides. There is also a section on ethyl ether as an anesthetic and another on crown ethers and their potential use to the biochemist.

Chapter 9 is on the chemistry of the carboxyl group. Oxidation of alcohols and aromatic hydrocarbons, carbonation of Grignard reagents, and hydrolysis of nitriles are the preparative methods discussed for carboxylic acids. The reactions of carboxylic acids include reduction, salt formation and acidity, formation of functional derivatives, and substitution. The reactions of the functional derivatives are presented as well. Mechanistically, ester formation and nucleophilic acyl substitution are discussed. The organophosphate insecticides are mentioned briefly. The reactivity of the functional derivatives compared to carboxylic acids is emphasized because a similar selectivity occurs in biochemical systems. The usefulness of malonic acid in the synthesis of carboxylic acids and barbiturates is included but can be omitted in a short course. This chapter concludes with a discussion of the chemicals we eat (food additives).

In Chapter 10 aldehydes and ketones are discussed. The preparative procedures for aldehydes include oxidation of primary alcohols, hydrolysis of geminal dihalides, and reduction of acid chlorides, while those for ketones include oxidation of secondary alcohols and Friedel-Crafts acylation. The nucleophilic addition reactions of carbonyl compounds are discussed, but generally the aldol condensation is omitted in a short course.

Chapter 11 discusses the chemistry of amines. Amines are synthesized by reduction of nitro compounds, reductive amination, reduction of nitriles, and the Hofmann degradation of amides. Reductive amination includes a theoretical implication in chemical evolution. The reactions of amines include salt formation and basicity, formation of diazonium compounds and their subsequent reactions, conversion into amides, including sulfonamide. There is

an application section on sulfanilamide and sulfa drugs. The section on heterocyclic amines can be omitted in a short course. The chapter includes a discussion on drugs such as hallucinogens, amphetamines, and narcotics.

A brief introduction to the chemical and physical methods used by organic chemists to deduce the structure of a molecule is presented in Chapter 12. The chemical tests for functional groups is summarized and outlined and the student is shown how to use infrared techniques for functional group identification and nuclear magnetic resonance for a more refined structure identification. A discussion on the use of classical and spectral techniques in the identification of a pheromone concludes the chapter.

Chapters 13 and 14 deal with biomolecules and biochemistry. The organic chemistry of biomolecules is divided into lipids, carbohydrates, and proteins. The topics of interest regarding lipids are fats, saponification, and the method by which a soap cleans. Brief introductions to waxes, phosphoglycerides, cerebrosides, and steroids are included but can be omitted in a short course. The role of vitamin A in the visual process and a proposal of the role of vitamin E as an antioxidant are described. The chemistry of carbohydrates is discussed in terms of the monosaccharide glucose, but sucrose, cellulose, and starch are also discussed. The last section on proteins includes the kinds and structures of amino acids, some of the reactions of amino acids, the Merrifield approach to the laboratory synthesis of peptides, and the primary and secondary structures of proteins (DNA and RNA).

Chapter 14 is an application of organic chemistry to the living system. It includes a discussion of enzyme catalyzed reactions, the function of the coenzyme, biochemical energetics, the Embden-Meyerhof pathway, Krebs' cycle, oxidation of fatty acids, and protein biosynthesis. The latter is developed in terms of the biosynthesis of normal and sickle-cell hemoglobin.

A number of people have given their time generously during the writing of this text. I would like to thank Clive Grant, David Pringle, and Charles DePuy for their comments and suggestions on early portions of this text. Gordon Tomasi was immensely helpful with the biochemistry chapters. John Idoux read the entire manuscript. His comments were valuable, appreciated, and always encouraging. I am grateful to Faye Magneson, who typed the entire manuscript, and also to many of my students who showed an interest in the text during the writing and rewriting stages. Finally, I am most grateful to my family, Jean, Steven, and Michael, who were so patient with me during the writing of this text.

James O. Schreck

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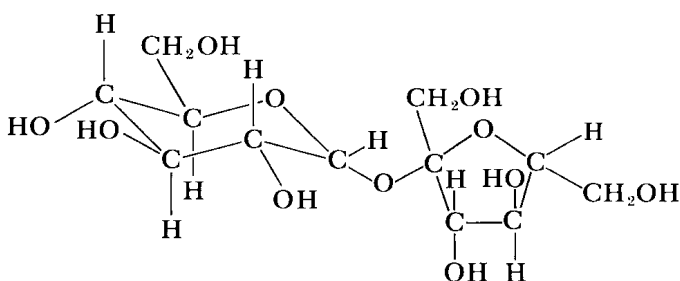
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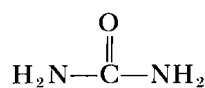
## chapter 1

### Some fundamental concepts

Up until the early 1800's organic chemistry was considered to be a study of those compounds isolated from living organisms, such as plants and animals. Sugar was considered to be an organic compound because it could be obtained from sugar cane or the sugar beet. Similarly, urea, which is the main end product of protein metabolism, formed in the liver of animals and excreted in the urine, was classified as an organic compound.

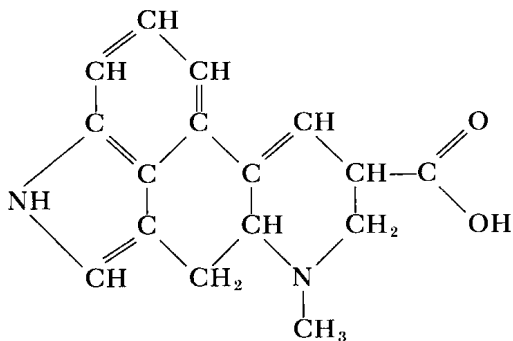


Sugar

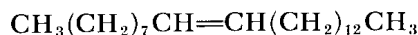


Urea

In 1828 the first organic compound was prepared in the laboratory without the use of a living organism. The organic compound synthesized was urea. Although organic compounds are often obtained from living organisms, chemists have now learned how to prepare a number of compounds found in nature. These include such diverse compounds as lysergic acid and *cis*-9-tricosene, the structures of which are as follows:



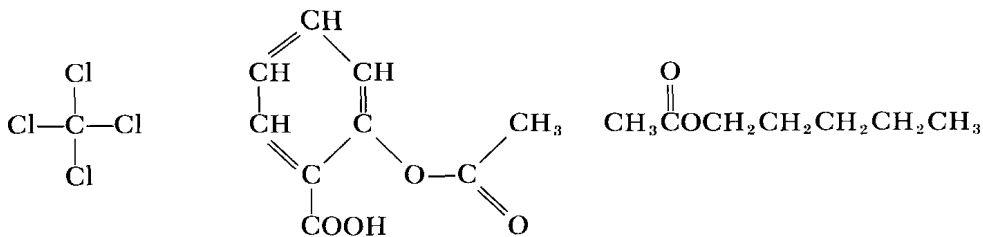
Lysergic acid: fungus  
disease of rye



*cis*-9-Tricosene: sex attractant  
of housefly

## 2 Organic chemistry: concepts and applications

In addition, chemists have synthesized many organic compounds not found in nature. Some of these compounds, such as carbon tetrachloride, acetylsalicylic acid, and amyl acetate, find application in our everyday life:

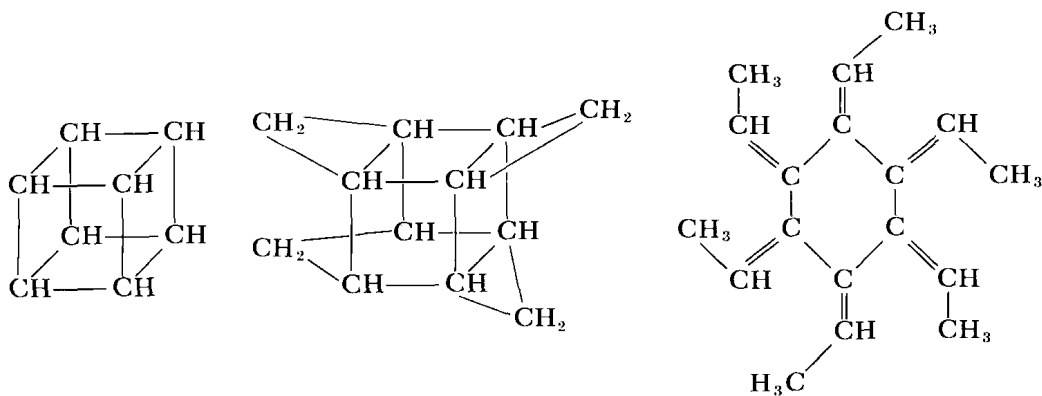


**Carbon tetrachloride:**  
dry cleaning solvent

**Acetylsalicylic acid:**  
aspirin

**Amyl acetate:**  
component of  
banana extract

Other interesting compounds not found in nature include cubane, asterane, and radialene, which have structures resembling their names. The synthesis of these compounds is a challenge to the organic chemist because of their unique structures:

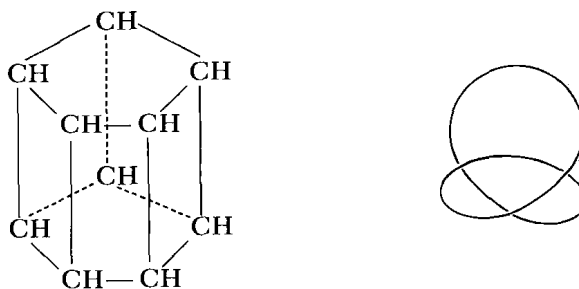


**Cubane**

**Asterane**

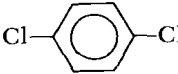
**Radialene**

Although millions of organic compounds are known, many millions more remain to be synthesized and studied. Following are two examples. The compound on the right is an example of a single chain of atoms that is knotted.



All these compounds have one feature in common. They contain the element carbon. Generally today, organic chemistry is considered to be a study of the chemistry of the compounds of carbon. However, some carbon

**Table 1-1**  
Classes of organic compounds

| <i>Class name</i> | <i>Class structure</i>   | <i>Example</i>  | <i>Common use or source</i>   |
|-------------------|--|---|---|
| Acid halide       | $-\text{COX}$ or $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{X} \end{array}$          | $\text{CH}_3\text{COCl}$  | Acetylating agent—used to introduce an acetyl group into a molecule |
| Alcohol           | $-\text{OH}^*$   | $\text{CH}_2\text{OHCH}_2\text{OH}$   | Antifreeze  |
| Aldehyde          | $-\text{CHO}$ or $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{H} \end{array}$          | $\text{C}_6\text{H}_5\text{CHO}$  | Oil of bitter almond  |
| Amide             | $-\text{CONH}_2$ or $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{NH}_2 \end{array}$    | $\text{H}_2\text{NCONH}_2$  | Barbiturate precursor   |
| Amine             | $-\text{NH}_2$   | $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$                                      | Used to synthesize nylon  |
| Carboxylic acid   | $-\text{COOH}$ or $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OH} \end{array}$        | $\text{CH}_3\text{COOH}$  | Vinegar   |
| Ester             | $-\text{COOR}^\dagger$ or $\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OR} \end{array}$ | $\text{CH}_3\text{COOC}_3\text{H}_{11}$   | Banana flavoring  |
| Ether             | $-\text{OR}$   | $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$   | Anesthetic  |
| Halogen compound  | $-\text{X}$  |  | Mothballs   |
| Hydrocarbons      |  |   |   |
| Alkane            | $-\text{C}-\text{C}-$ (single bonds only)  | $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$   | Component of gasoline   |
| Alkene            | $-\text{CH}=\text{CH}_2$   | $\text{CH}_2=\text{CCl}_2$  | Substance from which plastic wrap is made                           |
| Alkyne            | $-\text{C}\equiv\text{CH}$   | $\text{CH}\equiv\text{CH}^\ddagger$   | Oxyacetylene torch  |
| Ketone            | $-\text{COR}$ or $-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{R} \end{array}$          | $\text{CH}_3\text{COC}_2\text{H}_5$   | Fingernail polish remover   |
| Phenol            | $-\text{OH}^*$   | $\text{C}_6\text{H}_5\text{OH}$   | Antiseptic  |

\*The  $-\text{OH}$  group of an alcohol is chemically different from that of a phenol.

†The symbol R attached to the functional group represents an alkyl group, such as methyl ( $\text{CH}_3$ ) (see Chapter 2).

‡Acetylene ( $\text{CH}\equiv\text{CH}$ ) is a remarkably reactive substance, and almost every simple organic compound can be prepared from it. During World War II, Germany prepared large amounts of the simple organic compounds, such as ethanol, ethyl chloride, butadiene, and acetic acid, from acetylene and, as a result, became chemically independent of the rest of the world.

#### 4 Organic chemistry: concepts and applications

compounds, such as alkali carbonates (for example,  $\text{Na}_2\text{CO}_3$ ) and ferri-cyanides (for example,  $\text{K}_3\text{Fe}(\text{CN})_6$ ), are not considered to be organic compounds.

A study of organic chemistry is of interest to us because of the relationship of carbon compounds to life and life processes. Organic chemistry is the chemistry of plastics, gasoline, drugs, food, and clothing. The living system is made up of water and organic compounds. The study of biological processes, then, involves a study of organic chemistry. We will approach our study of organic chemistry from a study of the properties, reactions, and interrelationships of relatively simple organic compounds in relatively simple systems. We will then use these ideas to make predictions regarding more complex molecules in complex systems such as biological processes.

Organic chemists correlate the large amount of information about individual molecules by systematically dividing organic compounds into *classes*. Each class of organic compounds is characterized by a particular *functional group*. A functional group can be defined as a unique collection of chemically bonded atoms that displays a distinctive set of properties. All alkenes, for example, contain the carbon-carbon double bond,  $\text{C}=\text{C}$ . The reactions of alkenes are the reactions of the carbon-carbon double bond. Knowing the properties of the carbon-carbon double bond, one can make fairly good predictions regarding the physical and chemical properties of a new compound also known to be an alkene. For example, the carbon-carbon double bond in *cis*-9-tricosene would be expected to be very similar in properties to the carbon-carbon double bond in a simple alkene such as 1-butene ( $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ ).

The most common classes of organic compounds and the structure common to each class encountered in the study of organic chemistry are listed in Table 1-1.

#### Types of bonding: ionic and covalent

The molecules illustrated in the previous section consist of atoms held together by chemical bonds. It is important to understand how these bonds are formed. The nucleus of an atom is surrounded by electrons arranged in energy levels. The number of electrons in each energy level is limited. The first energy level is limited to two electrons, the second, to eight, and the third, to eighteen. The distribution of electrons in the energy levels for the first ten elements is shown in Table 1-2. The greatest stability for hydrogen is reached when the first energy level is full (two electrons) as in helium. In the case of the elements lithium through fluorine, the greatest stability is reached when the outermost energy level (second energy level in these elements) contains eight electrons as in neon. These atoms attain a stable electron configuration in one of two ways: by transfer of electrons from one atom to another or by sharing of electrons between atoms.

The transfer of electrons from one atom to another results in the formation of an ionic bond, as in the formation of beryllium oxide: