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University of Montana

and Joan S. Fessenden

**ORGANIC
CHEMISTRY**

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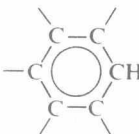
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Common Classes of Organic Compounds

Name	Functional group	General formula
Acid (or acyl) halide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CX} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCX} \end{array}$
Acid anhydride	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{COC}- \end{array}$	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{RCOCR} \end{array}$
Alcohol	$-\text{OH}$	ROH
Aldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CH} \end{array}$	RCHO
Alkane	none	RH
Alkene	>C=C<	$\text{R}_2\text{C=CR}_2$
Alkyl halide	$-\text{X}$	RX
Alkyne	$-\text{C}\equiv\text{C}-$	$\text{RC}\equiv\text{CR}$
Amide	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CN}< \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCNR}_2 \end{array}$
Amine	$-\text{N}<$	R_3N
Arene		ArH
Aryl halide	$-\text{X}$	ArX
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{COH} \end{array}$	RCO_2H
Ester	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{CO}- \end{array}$	RCO_2R
Ether	$-\text{O}-$	ROR
Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCR} \end{array}$
Nitrile	$-\text{C}\equiv\text{N}$	RCN
Phenol	$-\text{OH}$	ArOH
Sulfide	$-\text{S}-$	RSR
Sulfonic acid	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{SOH} \\ \parallel \\ \text{O} \end{array}$	RSO_3H
Thiol	$-\text{SH}$	RSH

Periodic Chart of the Elements

IA												VIIA					
1 H 1.0080												2 He 4.003					
IIA												VIIIA					
3 Li 6.940	4 Be 9.013											5 B 10.82	6 C 12.011	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.991	12 Mg 24.32											13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	18 Ar 39.944
IIIB		IVB		VB		VIB		VIIB		VIII		IB		IIB			
19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.880	48 Cd 112.41	49 In 114.82	50 Sn 118.70	51 Sb 121.87	52 Te 127.61	53 I 126.91	54 Xe 131.30
55 Cs 132.91	56 Ba 137.36	57 *La 138.92	72 Hf 178.50	73 Ta 180.95	74 W 183.86	75 Re 186.22	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.00	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 †Ac (227)	104 Ku (261)	105 Ha (260)													

* Lanthanides

58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm (147)	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99
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† Actinides

90 Th (232)	91 Pa (231)	92 U 238.07	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lw (257)
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Preface

To the beginning student, organic chemistry often appears to be a bewildering collection of unrelated structures, names, reactions, and mechanisms. This impression, of course, is false; but if students are to sort out these complexities, they must be able to distinguish between basic concepts and the extensions of these concepts. They must also be able to recognize the interrelationships between the various organic reactions. Therefore, a textbook should be more than just a source of information. It must guide the students and supply the framework for their learning. This is what we have attempted to provide in this book.

We have tried to explain each new topic and reaction thoroughly. Formulas and equations are annotated with explanatory notes. New reactions are compared and contrasted with reactions previously introduced. "Electron-pushing" mechanisms are shown wherever feasible. Each chapter is liberally supplied with worked-out sample problems and study problems for student solution. Chapter summaries are provided to reinforce the important points and to show similarities among groups of reactions.

In overall organization, our approach has been to develop first the concepts of structure and bonding and then discuss reactions and reaction mechanisms. Explanation of a few other points will point out why.

Introductory Material. Teaching organic chemistry was a rather simple affair 25 years ago. The traditional order of presentation was structural isomerism and nomenclature, followed by reactions. Today, in addition to these subjects, we must teach molecular orbital theory, stereochemistry, spectroscopy, and mechanisms, not to mention new reactions.

The inclusion of these new topics can impose a heavy "front load" of introductory material. We have made a special attempt to keep this to a minimum. Even so, we cannot, in good conscience, present a reaction and its mechanism on page 1. It is more important that the student first get a firm grasp on structure and bonding. These are the topics stressed in the first four chapters.

Chapters 1 and 2 are primarily reviews of atomic and molecular structure, along with electronegativity, hydrogen bonding, acid-base reactions, and molecular orbitals, presented for the most part in a graphical way. We have included the bonding of some simple nitrogen and oxygen compounds as a way of

introducing the concept of functional groups. A brief introduction to resonance theory is also presented here.

The student's introduction to structural isomerism and nomenclature comes in Chapter 3. Besides describing the nomenclature of alkanes, we briefly introduce the naming of a few other classes of compounds that will be encountered early in the book. Chapter 4, "Stereochemistry," contains more on structure: geometric isomerism, conformation, and chirality.

Organic Reactions. Since all of organic chemistry is interrelated, instructors must decide where and how to introduce organic reactions. If they start with free-radical halogenation, will this reaction assume the position of highest importance in the student's mind? Will such an approach place undue emphasis on hydrocarbon chemistry? We believe the answer to both these questions is "Yes." Therefore, our approach is to begin in Chapter 5 with the substitution and elimination reactions of alkyl halides (S_N2 , S_N1 , E1, and E2). This is followed by free-radical halogenation in Chapter 6.

There are several reasons why we introduce reactions and reaction mechanisms in this way instead of with the more traditional free-radical chlorination of methane.

- (1) Reactions involving pairs of electrons are more common in organic chemistry than those involving unpaired electrons.
- (2) The S_N2 reaction is a one-step reaction with a single transition state, and thus is ideal for introducing transition-state diagrams and reaction kinetics.
- (3) The S_N2 reaction, as well as the S_N1 , E1, and E2 reactions that follow, allows us to apply the stereochemical principles just covered in Chapter 4.
- (4) The presentation of the S_N1 reaction is a logical extension of the S_N2 reaction; therefore, steric hindrance and carbocations can be discussed early in the course.
- (5) Substitution and elimination reactions are excellent vehicles for introducing organic syntheses, and they lend themselves much better to beginning laboratory experiments than do free-radical reactions.

Alcohols, Chapter 7, follow the two chapters on alkyl halides because of the similarities in the substitution and elimination reactions of these two groups of compounds. After pausing in the presentation of organic reactions to introduce spectroscopy in Chapter 8, we continue with the chemistry of alkenes and alkynes (Chapter 9), benzene (Chapter 10), and carbonyl compounds (Chapters 11-13). The remaining chapters in the text are of more specialized interest. They may be included or omitted, in whole or in part, or presented in a different order as the instructor desires or has time for.

Throughout this text, our approach to reactions has been to show the similarities of the reactions of a particular group of compounds. For this reason, most reactions and their mechanisms are introduced in the sections on *reactions* of a class of compounds, instead of in the *preparation* section. Consequently, our preparation sections, such as 7.4 and 7.5 (preparations of alcohols and ethers), tend to be reviews of previously learned material. Although we feel these sections are good reinforcement, it is possible to delete them or present them elsewhere in your own presentation.

Spectroscopy. Spectroscopy is discussed as early as we think feasible—Chapter 8. By this time, the student has a working knowledge of structure, a few functional groups, and a few reactions. However, those who wish to do so may cover the spectroscopy chapter right after Chapter 4, as soon as the students are familiar with organic structures.

We have included only infrared and nuclear magnetic resonance spectroscopy in Chapter 8 because of their importance in structure determination. Sufficient background in the principles behind infrared and nmr spectroscopy is presented so that students can appreciate why spectra and structures are related, but the emphasis is on structure. Wherever appropriate after Chapter 8, we have inserted sections on the infrared and nmr characteristics of the compound classes being discussed. Structure-determination problems involving infrared and nmr spectra are included at the ends of many of these later chapters.

Ultraviolet and mass spectra are covered in Chapter 20. Our only reason for having two separate chapters on spectroscopy is to get the students quickly back into reaction chemistry. Both of these techniques can be presented along with infrared and nmr spectra if the instructor wishes. Ultraviolet and mass spectroscopy are designed to stand alone. One or both can be introduced whenever you think desirable.

Problems. We are firm believers in problem solving as an important part of learning organic chemistry, and we have included more than 1100 unsolved problems in the text. Within each chapter, a number of worked-out sample problems are included to illustrate the approach to problem solving and to provide further information. Often these sample problems are followed directly by study problems with answers at the end of the book. Many of these study problems are designed to relate previous material to the present discussion. Others are designed to test students on their mastery of new material.

The problems at the end of each chapter are of two types: drill problems and thought problems. Although their order of presentation tends to follow the chapter organization, they are graded in difficulty. The last several problems in each chapter should challenge even the best students. The *Study Guide with Solutions* that accompanies this text contains the answers to the chapter-end problems and also provides further explanation where appropriate.

Nomenclature. Many chemists think the time is overdue to switch from trivial names of organic compounds to systematic names. We agree. However, any issue of *Chemical and Engineering News* or any chemical catalog makes heavy use of trivial nomenclature. To be able to speak the language of chemists, a student needs to know that "acetone" and "propanone" are synonymous. Because of the present unsettled state of nomenclature, we have emphasized the IUPAC system, but we have not used it exclusively. Also used are some trivial names that are part of every organic chemist's vocabulary; for example, acetone and *t*-butyl chloride.

Our presentation of naming begins with a brief survey of systematic nomenclature in Chapter 3. The names presented there are those that the student will encounter again in chapters immediately following. The nomenclature for each class of compound is then discussed in more detail in later chapters. An appendix is included for those who wish additional material or a quick source of reference.

Synthesis. Opinions vary widely among instructors as to how much synthesis should be presented to students in an introductory course. Our formal discussions of organic synthesis are set off in separate sections and can therefore easily be emphasized or de-emphasized. These include Sections 5.12 (one-step syntheses); 7.18 (multistep syntheses); 10.12 (syntheses from benzene); and Chapter 14 (syntheses using enolates and enamines).

Topics of Specialized Interest. Organic chemistry lends itself to many fascinating sidelights. Unfortunately, what is of particular interest to one instructor may be of no interest to another. Although many authors have chosen to group topics of specialized interest into separate chapters, we prefer not to. Instead these subjects are placed where they follow logically from previous material. In this book, for example, electrocyclic reactions and polymers are found toward the end of Chapter 9 on alkenes and alkynes. In almost all cases, specialized topics will be found in separate sections so that they may be dealt with as the instructor deems best.

What sort of special-interest topics are included? Generally, ours fall into one of two categories: *organic chemistry for organic chemists* (e.g., electrocyclic reactions, polymers, carbenes, the cyclization of squalene) or *organic chemistry as it relates to the biological sciences* (e.g., the role of imines in transamination reactions, metabolism of ethanol, acetylcoenzyme A as an alkylating agent).

Bio-organic material. Many students in the introductory organic course are majoring in biological fields. Therefore, numerous sections and problems that are biological in nature have been included. We have selected material that is appropriate to the chemistry under discussion and that requires application of organic logic. Our intention is to show the close relationship between organic chemistry and the biological sciences.

Acknowledgments

A book of this magnitude requires the help of many people. We are indebted to the reviewers of the various drafts of the manuscript as it progressed from crude copy to its final form. First, we thank those who helped us formulate our ideas of topics to be included: James M. Bobbitt (Univ. of Connecticut); Harland D. Embree (San Jose State Univ.); John A. Katzenellenbogen (Univ. of Illinois); Robert R. Winkler (Ohio Univ.); and many others.

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Only someone who has typed a manuscript for an organic chemistry textbook can truly appreciate what this task entails! Therefore, we acknowledge our typists: Jackie Dunston, Karen Kougioulis, Susan Pirrong, Dianne Wilcoxson, and Carrie Avshalomov.

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