

# INTRODUCTION TO ORGANIC CHEMISTRY

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## CHEMICAL ABBREVIATIONS

Ac	acetyl, $\text{CH}_3\text{C}(=\text{O})\text{—}$
boc	<i>t</i> -butoxycarbonyl, $(\text{CH}_3)_3\text{COC}(=\text{O})\text{—}$
<i>n</i> -Bu	<i>n</i> -butyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
<i>t</i> -Bu	<i>t</i> -butyl, $(\text{CH}_3)_3\text{C—}$
cbz	benzyloxycarbonyl, $\text{C}_6\text{H}_5\text{CH}_2\text{OC}(=\text{O})\text{—}$
DCC	dicyclohexylcarbodiimide, $\text{C}_6\text{H}_{11}\text{N}=\text{C}=\text{NC}_6\text{H}_{11}$
DIBAL	di-isobutylaluminum hydride, $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlH}$
diglyme	bis-(2-methoxyethyl) ether, $(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}$
DMF	dimethylformamide, $(\text{CH}_3)_2\text{NCHO}$
DMSO	dimethyl sulfoxide, $(\text{CH}_3)_2\text{SO}$
DNP	2,4-dinitrophenyl, $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{—}$
Et	ethyl, $\text{CH}_3\text{CH}_2\text{—}$
glyme	1,2-dimethoxyethane, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$
HMPT	hexamethylphosphoric triamide, $[(\text{CH}_3)_2\text{N}]_3\text{PO}$
LAH	lithium aluminum hydride, $\text{LiAlH}_4$
LDA	lithium diisopropylamide, $\text{LiN}[\text{CH}(\text{CH}_3)_2]_2$
Me	methyl, $\text{CH}_3\text{—}$
PPA	polyphosphoric acid
THF	tetrahydrofuran, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$
TMS	tetramethylsilane, $(\text{CH}_3)_4\text{Si}$
Ts	<i>p</i> -toluenesulfonyl, $p\text{—CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{—}$

## EQUILIBRIA AND FREE ENERGY

$$\text{A} \rightleftharpoons \text{B} \quad K = \frac{[\text{B}]}{[\text{A}]}$$

$$\Delta G^\circ = -RT \ln K$$

<i>K</i>	%B	%A	$\Delta G^\circ$ at 25°C
			kcal mole <sup>-1</sup>
0.0001	0.01	99.99	+5.46
0.001	0.1	99.9	+4.09
0.01	0.99	99.0	+2.73
0.1	9.1	90.9	+1.36
0.33	25	75	+0.65
1	50	50	0
3	75	25	-0.65
10	90.9	9.1	-1.36
100	99.0	0.99	-2.73
1000	99.9	0.1	-4.09
10000	99.99	0.01	-5.46

## SYMBOLS FOR AMINO ACIDS

ala	alanine
arg	arginine
asp	aspartic acid
asn	asparagine
cys	cysteine
gln	glutamine
glu	glutamic acid
gly	glycine
his	histidine
ile	isoleucine
leu	leucine
lys	lysine
met	methionine
phe	phenylalanine
pro	proline
ser	serine
thr	threonine
trp	tryptophane
tyr	tyrosine
val	valine

*A Series of Books in Organic Chemistry*

*Andrew Streitwieser, Jr., Editor*

# ***INTRODUCTION TO***

# ***ORGANIC CHEMISTRY***

# PREFACE

With the dozens of textbooks now available for use in teaching organic chemistry, one may wonder why we add still another. The answer is simply that all of the existing textbooks we have used or studied have important limitations for instructional use. The present book was developed from draft versions used for several years in teaching the one-year course in organic chemistry (Chemistry 12AB, 112) at the University of California, Berkeley. As such it reflects some of the current trends in teaching organic chemistry.

In recent years, even the major's course in organic chemistry has become increasingly a service course for premedical students and others interested in biological sciences. We have recognized this trend by including examples and discussion of biological relevance, but we have tried to do so without slighting the chemistry major. One of the important aspects of organic chemical knowledge required by the nonmajor in subsequent careers is that of nomenclature. Yet, with the amount of material now covered, even in introductory studies of organic chemistry, nomenclature often gets short shrift in lectures. We have tried in this textbook to give adequate coverage to the naming of compounds, both with the IUPAC system and with common or trivial names that are actually used in practice in the real world.

Organic chemistry traditionally follows a year of general chemistry or "freshman chemistry," a course that has tended, in recent years, to emphasize physical chemistry at the expense of descriptive inorganic chemistry. To compensate for this development, we have included descriptions of the reagents that find important use in organic reactions. In fact, we have tried to present a feeling for chemicals as real stuff with physical attributes. This aspect of dealing with chemicals as materials is important to major and nonmajor alike; one reason many students are required to take organic chemistry courses is that they expect in their chosen careers to deal with, handle, and use organic compounds. One way in which we have tried to keep in touch with the real world in this textbook is the frequent use of actual reactions with reported yields. In many cases we have included some experimental details on how the reactions are actually run. This technique also serves the pedagogical purpose of emphasizing the important reactions to the student.

Another innovation has been the inclusion of stereo drawings, which make use of the capabilities of modern computer graphics. These figures require a stereo viewer for optimum use, and we expect that such viewers will become increasingly available in bookstores and familiar to students as the computer graphics techniques become useful in other textbooks. For physiological or psychological reasons some students cannot achieve three-dimensional perception, even with viewers. For such students the traditional use of molecular models and perspective diagrams must suffice. For most students the stereo diagrams emphasize the three-dimensional nature of organic structures and provide a useful supplement to the use of molecular models.

Throughout the text, we have made an effort to *explain* things—so much of organic chemistry reduces to Coulomb's law! Naturally, there is much use of reaction mechanisms. We have emphasized the use of resonance structures rather than molecular orbital theory. The knowledgeable reader will appreciate that we

## Preface

believe molecular orbital theory has an important application in organic chemistry, but he may be surprised at our belief that its role in an introductory course is quite limited.

The organization of this textbook differs somewhat from tradition. The growing tendency in organic chemistry courses to teach all the theory first has the unfortunate result of unduly delaying organic reactions. This type of organization may provide a logical organization of the science, but we believe it represents poor pedagogy. Instead, we have diffused theory through the text as needed. We start with alkanes because they form the basis of nomenclature, and proceed to halides, displacement reactions, alcohols, alkenes, alkynes, and carbonyl groups. Only after these important functional groups have been discussed are conjugated systems treated. Ring compounds and their conformations provide opportunity for reinforcement of some important reactions and lead naturally to glycols and hydroxy-carbonyl compounds and to the cyclic chemistry of epoxides, hemiacetals, and lactones. This discussion also provides a smooth introduction to carbohydrates. Condensation reactions, amines, amino acids, proteins, aromatic chemistry, and heterocycles conclude the organization. Chapter 36 consists of brief surveys of several additional topics that some instructors may wish to add as enrichment material. The book ends with a discussion of the chemical literature, complete with an abbreviated introduction to the use of Beilstein's *Handbuch der Organischen Chemie*.

Spectroscopy has become an increasingly important part of organic chemistry. We have introduced the four important spectroscopic methods as they become useful for individual functional groups. Nuclear magnetic resonance comes first and early because of its importance and because students like what they can achieve with nmr. Infrared spectroscopy is introduced after alcohols and multiple bonds are discussed. Mass spectroscopy follows the carbonyl group, and ultraviolet spectroscopy comes immediately after the introduction of conjugated systems.

The year course of organic chemistry at Berkeley consists of three quarters. The first quarter covers about Chapters 1 to 13. The second quarter finishes with Chapter 25, "Carbohydrates." In a two-semester sequence, the first semester should finish about Chapter 18 or 19. An advantage of starting the second semester with Chapter 19, "Organic Synthesis," is the opportunity it affords for reviewing important reactions covered in the first semester.

We are indebted to many people for their essential help in creating this text. We learned much from and appreciate the feedback we got from students who used early editions of the manuscript in our courses. The cmr spectra in Chapter 10 were measured by James Shoolery of Varian Associates. Infrared spectra were obtained on a Perkin-Elmer 735 infrared spectrometer by Robert Hannah, Ron Anderson, Mary Zeller, and Mark Juszli of Perkin-Elmer. John T. Dickman of Chemical Abstracts Service critically evaluated Chapter 37 and granted permission to reproduce illustrative material from *Chemical Abstracts*. Several of our students have prepared special compounds for the determination of spectra—Edward Binkley, Phyllis Toczko, and Lee Kozar. We are also grateful to numerous individuals who have supplied information, read portions of the text, and offered their criticism and suggestions—Joseph Lavigne, Joseph Casanova, Heinz Koch, Gene Ziegler, Donald Noyce, Henry Rapoport, Douglas Browne, Steven Kent, and David Streitwieser. Many of the computer-drawn stereo plots were prepared with the assistance of Peter Owens and John McKelvey. Others were reproduced from the chemical literature, cited with the permission and cooperation of the authors. Several of the plots used coordinates supplied by Professor Norman Allinger.

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# CHAPTER 1

## *Introduction*

Although chemistry did not emerge as a coherent science until the seventeenth century, its roots extend back into antiquity. Chemical changes were probably first brought about by paleolithic man when he discovered that he could make fire and use it to warm his body and roast his food. Being a curious and a resourceful creature, man observed and exploited other natural phenomena. By neolithic times he had discovered such arts as smelting, glass making, the dyeing of textiles, and the manufacture of beer, wine, butter, and cheese.

Matter and changes of matter were not systematically discussed in a theoretical sense until the period of the Greek philosophers, beginning in about 600 B.C. The popular theory that emerged during this period saw all matter as being made up of the four “elemental” substances: fire, earth, air, and water. For a time, the atomist school, of which Democritus was the chief spokesman, gained popularity. In this theory, all matter was considered to be made up of hypothetical particles called atoms, of which there were assumed to be but a finite number of different kinds. Although the atomists held sway for several centuries, the notion was highly speculative, being based on nothing directly observable. The demise of this theory was foreshadowed when it was rejected by the highly respected Aristotle; its burial was assured with the advent of stoicism and the subsequent rise of the popular religious movements in the Western world. The idea of fundamental particles was not resurrected for almost two millenia.

Some time around the time of Christ, the Greek philosophers hit upon the idea of changing (or “transmuting”) base metals such as lead and iron into gold and silver. Although alchemy was first practiced in a serious sense by the Greeks, it quickly spread to other cultures and continued as a lively discipline throughout the world for over a thousand years. This alchemical period has often been put down as a “dark age” of science. However, one must recognize that there is nothing inherently wrong with the notion that one metal may be transformable into another. Chemistry is, in fact, based upon changes in the state of matter. The alchemists had no way of recognizing the elemental nature of the metals with which they dealt.

Although they were uniformly unsuccessful in their quest for the philosopher’s stone, the alchemists contributed a great deal to the technology of handling matter. Not only did they develop numerous processes for the production of relatively pure compounds but they also invented tools and apparatus. Many of these inventions persist in general form to the present day—beakers, flasks, funnels, mortars, crucibles. Perhaps the most important invention of alchemy was the still.

The important technique of distillation was probably discovered by the early Greek alchemists when they noticed condensate on the lid of a vessel in which some liquid was being heated. It was only a short step from this observation to the realization that this technique could be used to separate volatile substances from nonvolatile animal and vegetable matter. Although the still was quite inefficient in its infancy, its design improved steadily. By 1300, actual fractionation was being practiced, and alcoholic distillates of fairly high alcohol concentration were available. The production of whiskey and brandy became an established industry in short order.