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# ***Fundamentals of Organic Chemistry***

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***Dedicated to the University***

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When a textbook is written in a field that has reached maturity, such as the field of organic chemistry, it is inevitable that other textbooks and compendia provide invaluable sources of information in its preparation. Our first acknowledgment, therefore, is to the many chemists who have preceded us in this task of authorship and from whose efforts we have drawn innumerable facts, theories, and ideas.

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Other professional colleagues read smaller segments of the text, segments dealing with areas of their particular expertise. Included in this group of critics are Professors Robert Barker (University of Iowa), Robert G. Bergman (California Institute of Technology), Oscar P. Chilson (Washington University), Ernest L. Eliel (University of North Carolina), Peter P. Gaspar (Washington University), Lindsay Helmholtz (Washington University), Alfred G. Hortmann (Washington University), Joseph L. Kurz (Washington University), and David Lipkin (Washington University). To these individuals we are indebted for advice and corrections which were invaluable in improving the level of accuracy and clarity in various portions of the text.

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Finally, acknowledgment is made to those who contributed in less direct ways. Between the initial scribbblings of the authors and the final manuscript for the publisher came numerous intervening editions, each requiring long and careful secretarial effort. Among the several individuals who helped in this respect, special commendation goes to Renate Keith, whose rapid and accurate typing materially aided this project. Two other individuals who were also indispensable to the writing of the text are Dr. Frank Williamson and Norma Frick, whose collective willingness and ability to undertake administrative responsibility made it possible for one of the authors (CDG) to work on the book while at the same time acting, ostensibly, as chairman of a department.

To all of the many people who, in these various ways, have helped with the preparation of this textbook we express our deep gratitude. Because of their contributions it is a much better book than it might otherwise have been.

## Preface

Over the course of the last 150 years organic chemistry has grown from a vulnerable infant to a mature and robust giant. To comprehend in detail all of its many facets now requires years of study. Many textbooks have been written to provide the starting point for this study, each of them with the intention of capturing the essence of the giant in a few thousand well-chosen words. The present book is no exception in this respect, for we hope to give the reader some understanding and appreciation of *all* of the facets of organic chemistry as well as a reasonably detailed comprehension of those particular areas that are of special interest and importance to students preparing to enter scientific professions in which a knowledge of organic chemistry is an essential ingredient. To achieve this, the subject matter has been organized in a spiral fashion in which there are several turns to the spiral.

Among the many problems attending the presentation of any large body of knowledge, the two that loom largest are those of where to start and how to arrange the material. To some extent the second of these, the problem of arrangement, is solved by the nature of the material itself. There is a considerable degree of linearity to the subject matter of organic chemistry, one idea building on another, so certain patterns of presentation automatically emerge. However, there is also a certain degree of circularity, topic C requiring a knowledge of topic B, topic B requiring a knowledge of topic A, but topic A requiring a knowledge of topic C. To minimize the difficulties arising from this situation, the present text surveys all of the basic principles of organic chemistry quickly and concisely and then, building from this foundation, reconsiders certain segments in greater detail. While the problem of circularity remains, it is minimized by reducing the size of the circle or, perhaps more accurately, by replacing one big circle by a series of smaller circles. With the spiral scheme for organizing the subject matter of organic chemistry, the reader can perceive the overall pattern into which fit the many facts of the field faster than he could with the strictly linear presentation.

Part I of the book presents a general survey of organic chemistry and deals with the structure, nomenclature, stereochemistry, physical properties, and chemical properties of the important classes of organic compounds. Although focusing principally on the structural aspects of compounds, it gives an overall view of the entire field of organic chemistry and provides the framework to which Part II adds detail, especially with respect to the

mechanisms, scope, and limitations of organic reactions. To borrow from the language of psychology, the approach to the learning of organic chemistry that is used in this text might be designated as "gestalt" in character, the term "gestalt" referring to a system in which the phenomena are integrated in such a fashion as to constitute a functional unit with properties not derivable from its parts—more colloquially referred to as the whole being greater than the sum of its parts. Thus, Part II requires Part I for its foundation, but Part I becomes strengthened through a study of Part II, each part reinforcing the other.

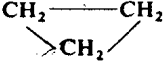
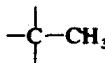
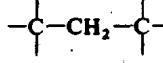
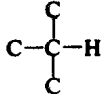
Part III presents the organic chemistry of natural products, a topic of special interest to those who will eventually deal, in one form or another, with living systems. The emphasis in Part III is primarily on the structure of natural products, and the material in Part I alone provides an adequate preparation for understanding it. Some readers and teachers, therefore, may choose to change the sequence and consider some or all of Part III immediately after Part I, deferring Part II to a later point. Both sequences of presentation have been class-tested during the past several years, and the book appears to be equally well suited to either alternative.

Part IV treats several topics in a more advanced manner than Parts I, II, and III and provides a transition to the material that one encounters in higher-level courses in organic chemistry. It is directed primarily to those who plan to continue their study of organic chemistry. Except in the most rapidly paced elementary courses, most of this material would not be included in the two semester sequence.

The intention of this book, which is a teaching text rather than an encyclopaedic reference book, is to furnish a well-documented survey of modern organic chemistry and a secure foundation for more advanced study of organic chemistry. Encyclopaedic textbooks are available, and these, along with advanced treatises and original articles in the chemical literature, are recommended supplementary reading. Students planning to enter chemically oriented professions are urged to actively explore these additional sources of information, many of which are cited at the end of each chapter.

An often-voiced sentiment of students asserts that "organic chemistry is simply a memory course." That it does, indeed, exercise one's ability to remember cannot be denied. There are few, if any, intellectual endeavors that don't make considerable demands on this remarkable faculty of man. But the idea that it is *simply* a feat of memory is, in our experience, quickly dispelled by the spiral presentation of the subject matter. Since the spiral approach allows the student to quickly perceive the "grand plan" and, as a consequence, to be able quite soon in the study of organic chemistry to appreciate the logical connections between the facts that are presented, the apparent arbitrariness of having to remember the fact disappears. The process of committing the fact to memory becomes logical rather than rote and, concomitantly, less onerous. For many students it even becomes an enjoyable experience, and we hope that this will be true for the readers of this textbook. *Bon voyage!*—C. DAVID GUTSCHE, DANIEL J. PASTO.

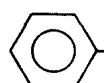
NMR CHARACTERISTICS OF VARIOUS MOLECULAR GROUPINGS

Compound Type	$\delta$ Value	Compound Type	$\delta$ Value
$(\text{CH}_3)_4\text{Si}$	0.00	Halogen- $\text{CH}_3$	$3.5 \pm 1.2$
$\text{CH}_2-\text{CH}_2$ 	0.22	$\text{O}-\text{CH}_3$	$3.6 \pm 0.3$
$\text{CH}_4$	0.23	$\text{RO}-\text{H}$	0.5-5.5
$-\text{C}-\text{CH}_3$ 	$1.1 \pm 0.1$	$=\text{CH}_2$ and $=\text{CHR}$	4.5-7.5
$-\text{C}-\text{CH}_2-\text{C}-$ 	$1.3 \pm 0.1$	$\text{Ar}-\text{H}$	$7.4 \pm 1.0$
$\text{C}-\text{C}-\text{H}$ 	$1.5 \pm 0.1$	$\text{ArO}-\text{H}$	4.5 - 9.0
$\text{RNH}_2$	0.6-4.0	$\text{RCONH}_2$	$8.0 \pm 0.1$
$=\text{CCH}_3$	$1.75 \pm 0.15$	$\text{RCHO}$	$9.8 \pm 0.3$
$\equiv\text{CCH}_3$	$1.80 \pm 0.15$	$\text{RCO}_2\text{H}$	$11.6 \pm 0.8$
$\text{Ar}-\text{CH}_3$	$2.35 \pm 0.15$	$\text{RSO}_3\text{H}$	$11.9 \pm 0.3$
$\equiv\text{CH}$	$1.8 \pm 0.1$		

BOND ENERGIES IN KCAL/MOLE FOR VARIOUS TYPES OF SINGLE, DOUBLE, AND TRIPLE BONDS

	Homopolar Bond		Bond to Hydrogen		Bond to Carbon	
Hydrogen :	H—H	104	H—H	104	C—H	99
Halogen :	F—F	37	H—F	135	C—F	116
	Cl—Cl	58	H—Cl	103	C—Cl	81
	Br—Br	46	H—Br	87	C—Br	68
	I—I	36	H—I	71	C—I	51
Oxygen :	O—O	35	H—O	111	C—O	85
	O=O	119			C=O	179
					C≡O	256
Nitrogen :	N—N	39	H—N	93	C—N	73
	N=N	100			C=N	147
	N≡N	226			C≡N	213
Carbon :	C—C	83	Bond energies for specific types of C—H bonds			
	C=C	146				
	C≡C	200				

Bond energies for specific types of C-H bonds

$\text{H}_3\text{C}-\text{H}$ 102	$-\text{C}-\text{H}$ 90
$\text{H}_2\text{C}-\text{H}$ 97	$\text{C}=\text{H}$ 106
	$\equiv\text{C}-\text{H}$ 121
$\text{HC}-\text{H}$ 94	 -H 112

**INFRARED ABSORPTION BANDS USEFUL FOR STRUCTURAL ASSIGNMENTS\***

**X-H Stretching Deformation Bands:**

O-H	3650-3100 (2.74-3.22)
N-H	3550-3100 (2.82-3.22)
$\equiv\text{C-H}$	3330 (3.00)
$=\text{C-H}$	3085-3025 (3.24-3.31)
Ar-H	3030 (3.30)
$\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array}$	2960-2870 (3.38-3.49)
S-H	2500 (4.00)

**X=Y Stretching Deformation Bands:**

$\text{C}=\text{O}^b$	1850-1650 (5.40-6.05)
$\text{C}=\text{NR}^b$	1690-1640 (5.92-6.10)
$\text{C}=\text{C}^b$	1680-1600 (5.95-6.25)
$\text{N}=\text{N}$	1630-1575 (6.14-6.35)
$\text{N}=\text{O}$	1650-1500 (6.06-6.66)



1600-1450 (6.25-6.90)  
(four bands)

**X $\equiv$ Y and X=Y=Z Stretching Bands:**

$\text{C}\equiv\text{N}$	2260-2240 (4.43-4.46)
$\text{RC}\equiv\text{CR}'$	2260-2190 (4.43-4.56)
$\text{RC}\equiv\text{CH}$	2140-2100 (4.68-4.76)
$\text{C}=\text{C}=\text{O}$	2170-2130 (4.61-4.70)
$\text{C}=\text{C}=\text{C}$	1975-1950 (5.07-5.13)

**C-H Bending Deformation Bands in the Fingerprint Region:**

$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{R} \end{array}$	$\sim 970$ (10.30)
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$	$\sim 900$ (11.11)
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$	$\sim 825$ (12.11)
$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	$\sim 670$ (14.90)
$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	$\sim 1000$ and $900$ (10.0 and 11.1)

\* Data are given in wave numbers ( $\text{cm}^{-1}$ ) and, in parentheses, micrometers ( $\mu\text{m}$ ).

<sup>b</sup> Conjugation with a  $\text{C}=\text{C}$  or aryl group lowers the frequency about  $30 \text{ cm}^{-1}$



$pK_a$  VALUES FOR THE REACTION  $AH + B \rightleftharpoons BH^+ + A^-$  (ACID DISSOCIATION CONSTANTS)





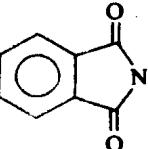
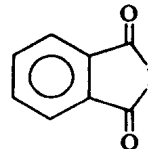
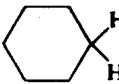
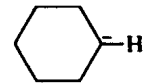
Reaction	$pK_a$	Reaction	$pK_a$
$FSO_3H + B \rightleftharpoons BH^+ + FSO_3^-$	-12	$C_6H_5SH + B \rightleftharpoons BH^+ + C_6H_5S^-$	7.8
$HI + B \rightleftharpoons BH^+ + I^-$	-10	$C_6H_5CO_3H + B \rightleftharpoons BH^+ + C_6H_5CO_3^-$	8.2
$HClO_4 + B \rightleftharpoons BH^+ + ClO_4^-$	-10	$CH_3COCH_2COCH_3 + B \rightleftharpoons BH^+ + CH_3CO\bar{C}HCOCH_3$	9.0
$H_2SO_4 + B \rightleftharpoons BH^+ + HSO_4^-$	-9	$HCN + B \rightleftharpoons BH^+ + CN^-$	9.1
$\begin{array}{c} H \\   \\ R-C=O^+H + B \rightleftharpoons BH^+ + \\   \\ R \end{array} \begin{array}{c} H \\   \\ R-C=O \\   \\ R \end{array}$	-8	$C_6H_5OH + B \rightleftharpoons BH^+ + C_6H_5O^-$	10.0
$HCl + B \rightleftharpoons BH^+ + Cl^-$	-7	$HCO_3^- + B \rightleftharpoons BH^+ + CO_3^{2-}$	10.2
$\begin{array}{c} R \\   \\ R-C=O^+H + B \rightleftharpoons BH^+ + \\   \\ R \end{array} \begin{array}{c} R \\   \\ R-C=O \\   \\ R \end{array}$	-7	$CH_3NH_3^+ + B \rightleftharpoons BH^+ + CH_3NH_2$	10.4
$\begin{array}{c} R \\   \\ R-O^+-H + B \rightleftharpoons BH^+ + \\   \\ R \end{array} \begin{array}{c} R \\   \\ R-O \\   \\ R \end{array}$	-3.5	$CH_3CH_2SH + B \rightleftharpoons BH^+ + CH_3CH_2S^-$	10.5
$\begin{array}{c} H \\   \\ H-O^+-H + B \rightleftharpoons BH^+ + \\   \\ H \end{array} \begin{array}{c} H \\   \\ H-O \\   \\ H \end{array}$	-1.7	$CH_3NO_2 + B \rightleftharpoons BH^+ + \bar{C}H_2NO_2$	11.0
$HNO_3 + B \rightleftharpoons BH^+ + NO_3^-$	-1.3	$CH_3COCH_2CO_2C_2H_5 + B \rightleftharpoons BH^+ + CH_3CO\bar{C}HCO_2C_2H_5$	11.0
$C_6H_5SO_3H + B \rightleftharpoons BH^+ + C_6H_5SO_3^-$	-0.6	$CCl_3CH_2OH + B \rightleftharpoons BH^+ + CCl_3CH_2O^-$	12.2
$CF_3CO_2H + B \rightleftharpoons BH^+ + CF_3CO_2^-$	0	$CH_2(CO_2C_2H_5)_2 + B \rightleftharpoons BH^+ + \bar{C}H(CO_2C_2H_5)_2$	13.0
$CCl_3CO_2H + B \rightleftharpoons BH^+ + CCl_3CO_2^-$	0.9	 + B $\rightleftharpoons$ BH <sup>+</sup> + 	14.0
$Cl_2CHCO_2H + B \rightleftharpoons BH^+ + Cl_2CHCO_2^-$	1.3	$CH_3CONH_2 + B \rightleftharpoons BH^+ + CH_3CONH^-$	15.0
$H_3PO_4 + B \rightleftharpoons BH^+ + H_2PO_4^-$	2.1	$CH_3OH + B \rightleftharpoons BH^+ + CH_3O^-$	15.5
$ClCH_2CO_2H + B \rightleftharpoons BH^+ + ClCH_2CO_2^-$	2.8	$H_2O + B \rightleftharpoons BH^+ + HO^-$	15.7
$HF + B \rightleftharpoons BH^+ + F^-$	3.2	$CH_3CH_2OH + B \rightleftharpoons BH^+ + CH_3CH_2O^-$	17
$HCO_2H + B \rightleftharpoons BH^+ + HCO_2^-$	3.7	$(CH_3)_3COH + B \rightleftharpoons BH^+ + (CH_3)_3CO^-$	19
$C_6H_5CO_2H + B \rightleftharpoons BH^+ + C_6H_5CO_2^-$	4.2	$CH_3COCH_3 + B \rightleftharpoons BH^+ + CH_3COCH_2^-$	20
$C_6H_5\dot{N}H_3 + B \rightleftharpoons BH^+ + C_6H_5NH_2$	4.6	$C_6H_5C\equiv CH + B \rightleftharpoons BH^+ + C_6H_5C\equiv C^-$	21
$CH_3CO_2H + B \rightleftharpoons BH^+ + CH_3CO_2^-$	4.8	$(C_6H_5)_2NH + B \rightleftharpoons BH^+ + (C_6H_5)_2N^-$	23
 + B $\rightleftharpoons$ BH <sup>+</sup> + 	5.2	$HC\equiv CH + B \rightleftharpoons BH^+ + HC\equiv C^-$	26
$H_2CO_3 + B \rightleftharpoons BH^+ + HCO_3^-$	6.5	$C_6H_5NH_2 + B \rightleftharpoons BH^+ + C_6H_5NH^-$	27
$H_2S + B \rightleftharpoons BH^+ + HS^-$	7	$(C_6H_5)_3CH + B \rightleftharpoons BH^+ + (C_6H_5)_3C^-$	31.5
$O_2N-\text{C}_6\text{H}_4-\text{OH} + B \rightleftharpoons BH^+ + O_2N-\text{C}_6\text{H}_4-\text{O}^-$	7.2	$(C_6H_5)_2CH_2 + B \rightleftharpoons BH^+ + (C_6H_5)_2CH^-$	33
 + B $\rightleftharpoons$ BH <sup>+</sup> + 	7.4	$CH_3CH_2NH_2 + B \rightleftharpoons BH^+ + CH_3CH_2NH^-$	33
		$C_6H_5CH_3 + B \rightleftharpoons BH^+ + C_6H_5CH_2^-$	35
		$NH_3 + B \rightleftharpoons BH^+ + NH_2^-$	36
		$H_2C=CH_2 + B \rightleftharpoons BH^+ + H_2C=CH^-$	36
		$CH_4 + B \rightleftharpoons BH^+ + CH_3^-$	40
		$CH_3CH_3 + B \rightleftharpoons BH^+ + CH_3CH_2^-$	42
		$C_6H_6 + B \rightleftharpoons BH^+ + C_6H_5^-$	42
		 + B $\rightleftharpoons$ BH <sup>+</sup> + 	45

TABLE OF ATOMIC WEIGHTS

	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Mass</i>		<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Mass</i>
Actinium	Ac	89	227*	Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95	243*	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	237*
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85	210*	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97	247*	Nobelium	No	102	255*
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994
Boron	B	5	10.811	Palladium	Pd	46	105.4
Bromine	Br	35	79.909	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	242*
Californium	Cf	98	251*	Polonium	Po	84	210*
Carbon	C	6	12.01115	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.907
Cesium	Cs	55	132.905	Promethium	Pm	61	145*
Chlorine	Cl	17	35.453	Protactinium	Pa	91	231*
Chromium	Cr	24	51.996	Radium	Ra	88	226*
Cobalt	Co	27	58.9332	Radon	Rn	86	222*
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96	247*	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	254*	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Rutherfordium**		104	260*
Europium	Eu	63	151.96	Samarium	Sm	62	150.35
Fermium	Fm	100	257*	Scandium	Sc	21	44.956
Fluorine	F	9	18.9984	Selenium	Se	34	78.96
Francium	Fr	87	223*	Silicon	Si	14	28.086
Gadolinium	Gd	64	157.25	Silver	Ag	47	107.870
Gallium	Ga	31	69.72	Sodium	Na	11	22.9898
Germanium	Ge	32	72.59	Strontium	Sr	38	87.62
Gold	Au	79	196.967	Sulfur	S	16	32.064
Hafnium	Hf	72	178.49	Tantalum	Ta	73	180.948
Hahnium**	Ha	105	260*	Technetium	Tc	43	99*
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium	Lr	103	256*	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.312	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9381	Zirconium	Zr	40	91.22
Mendelevium	Md	101	256* (?)				

\* Mass number of isotope of longest known half-life.

\*\* Names and symbols not officially approved.

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## IV

### ***Special Topics***

## **PART I**

# ***A Survey of Organic Chemistry: The Structure of Organic Compounds***

Part I, as indicated in the Preface, provides a general survey of organic chemistry and includes discussions of structure, nomenclature, stereochemistry, physical properties, and chemical properties of the important classes of organic compounds. Following Chapter 1, which presents a capsule survey and history of organic chemistry, Chapters 2–8 deal with the carbon frameworks of organic compounds. Chapters 9–17 then consider the chemistry of the various compounds that are formed when functional groups are attached to these carbon frameworks. Chapter 18 furnishes a summary of some of the topics covered in the first 17 chapters, including tables of physical properties, summaries of the rules of nomenclature, and guidelines for structure elucidation and synthesis. Part I is concluded by a detailed chapter on stereochemistry, the elementary principles of which are first introduced in Chapter 3.

The relative emphasis placed on the various topics covered in Part I will vary from one reader to another and from one instructor to another. Perhaps most sensitive in this respect is the material in Chapter 6 dealing with the spectral properties of organic compounds, the extent to which it is covered depending on the aims and goals of the particular student and the particular course. Pre-medical students and students in the Humanities, who are primarily interested in acquiring an overall appreciation of organic chemistry, may be less inclined to delve into the intricacies of spectra than chemistry majors, biochemistry majors, and others who will eventually use organic chemistry as a practical tool in their work. The book has been written in such a fashion that spectra can be emphasized, if that is the reader's and instructor's choice, or be dealt with rather cursorily, or even omitted entirely without substantially interfering with the subsequent presentation.

The suggestion that spectral properties can be deemphasized does not mean that they are trivial or incidental. On the contrary, spectral measurements are an absolutely essential ingredient of modern organic chemistry as it is conducted in the laboratory, and for persons who intend to use organic chemistry in a

practical fashion it is necessary that a good working knowledge of spectroscopy be acquired. But, to be able to read and appreciate most of the material in this book one does not have to be conversant with spectra. Clearly, though, the more one knows about all the facets of a subject, the deeper is his overall understanding and the greater is his capacity for savoring the nuances of the subject.

*Part I*  
*A Survey of*  
*Organic Chemistry:*  
*The Structure of*  
*Organic Compounds*

## Chapter 1

# *The scope of organic chemistry*

Organic chemistry gives me the impression of a primeval tropical forest, full of the most remarkable things.

FRIEDRICH WÖHLER (1840)

Several centuries ago, when alchemists still dominated the chemical scene, it was thought that certain compounds found in nature required a mysterious "vital force" for their synthesis. Compounds of this type came to be called *organic*, and the study of them came to be called *organic chemistry*. Although the notion of a "vital force" has long since been discarded and although most of the compounds that today we class as "organic" have been synthesized in the laboratory rather than in nature, the use of the term has persisted.

The "modern" era of organic chemistry began to take shape at the beginning of the nineteenth century. Even in its infancy organic chemistry attracted the attention of some of the greatest chemists of the day and inspired their awe. Friedrich Wöhler, who played a key role in guiding the discipline in its earliest days, commented that "organic chemistry is full of the most remarkable things, a monstrous and boundless thicket . . ." In the century and a half that has elapsed since Wöhler's time many more remarkable things have been added to organic chemistry, and we might suppose that today the thicket is even more monstrous and boundless than ever. Fortunately, the reverse is true. Although the territory that organic chemistry now encompasses is indeed large, its boundaries are sufficiently well defined and its terrain sufficiently well perceived that an understanding and appreciation of its details is easily within the grasp of everyone; the boundless has become bounded and the thicket has been carefully pruned.

To gain a brief overall glimpse of the territory called organic chemistry, let us trace the development of our knowledge of a particular organic compound that has probably been known to man since the dawn of recorded history, the compound that we now call acetic acid. Acetic acid is the principal nonaqueous component of vinegar, which derives its name from a combination of the French words *vin* ("wine") and *aigre* ("sour"), i.e., "sour wine," indicating that one of the natural sources of vinegar is wine that has turned sour as the result of the

### 1.1

#### ***A Capsule View of the Scope of Organic Chemistry***

action of certain microorganisms. For centuries, vinegar has been used for flavoring and preserving foods. It was prescribed by Hippocrates in ancient Greece as a medicine and was used during the American Civil War in the treatment of scurvy. Today acetic acid is produced on an enormous scale, the United States alone manufacturing over 2 billion pounds in 1971. In addition to the continued culinary use of vinegar, acetic acid now finds application in the manufacture of a host of useful materials, including fibers, fabrics, plastics, and medicines. It is a typical organic compound whose chemistry we shall now quickly explore.

Sometime near the beginning of the present millenium, a medieval scholastic and early alchemist named Geber discovered that vinegar can be distilled and that the major fraction of the distillate is water. He also discovered that a smaller fraction is obtained, which is a stronger, more concentrated vinegar than the original material. For several hundred years, however, this early experiment went unheeded. Not until the seventeenth and eighteenth centuries was distillation equipment sufficiently improved to allow more highly concentrated vinegar solutions to be prepared. Finally, in 1798 Tobias Lowitz combined distillation with other means of purification and succeeded in preparing a water-free sample of vinegar, which he obtained as a crystalline solid melting at  $16^{\circ}\text{C}$ . This material acquired the German name *eisessig*, meaning "solid vinegar," and it is the compound that we refer to in English as acetic acid. With the preparation of a pure sample of acetic acid, the first phase in the study of the organic chemistry of this compound was complete, *viz.*, the separation of vinegar into its component parts (about 94 % water and 6 % acetic acid) followed by the purification of each of these constituents.

With a pure sample of acetic acid available, it then became possible to carry out the next phase of the investigation, *viz.*, the determination of the elemental composition of the compound. Building on Antoine Lavoisier's contributions to analytical chemistry at the end of the eighteenth century, Jöns Jacob Berzelius added improvements springing from his own fertile mind, and in 1814 he succeeded in establishing that acetic acid contains carbon, hydrogen, and oxygen atoms in the ratio 1 : 2 : 1; in other words, he determined that the *empirical formula* for acetic acid is  $\text{CH}_2\text{O}$ . Let us see how he did this.

Commencing his analysis by carefully weighing out a sample of pure acetic acid, Berzelius then burned the sample (combusted it), thereby converting it to carbon dioxide and water. By weighing the carbon dioxide and water that were formed and by knowing the weight of the original sample, he was able to determine the relative amounts of carbon, hydrogen, and oxygen present in acetic acid by means of the following procedures. Let us assume, for example, that the weight of the acetic acid sample was 3.26 g and that this produced 4.74 g of carbon dioxide and 1.92 g of water upon combustion.\* From these data, the

---

\* With the equipment available to Berzelius it was necessary to trap the carbon dioxide and water in weighing tubes filled with appropriate reagents. For example, magnesium perchlorate traps water, and sodium hydroxide traps carbon dioxide, as indicated in the following picture of a typical apparatus for carrying out an analysis of the type described. In a modern combustion analysis, milligram rather than gram amounts of sample would be used; e.g., a 3.26 mg sample of acetic acid would produce 4.74 mg of carbon dioxide and 1.82 mg of water.



percentage of carbon, hydrogen, and oxygen in acetic acid can be calculated as follows:

Section 1.1  
A Capsule View of the  
Scope of Organic Chemistry

$$\text{wt. of C} = \text{wt. of CO}_2 \left( \frac{\text{at. wt. of C}}{\text{mol. wt. of CO}_2} \right) = (4.74) \frac{12}{44} = 1.29$$

$$\left( \frac{\text{wt. of C}}{\text{wt. of sample}} \right) 100 = \left( \frac{1.29}{3.26} \right) 100 = 39.6\% \text{ C}$$

$$\text{wt. of H} = \text{wt. of H}_2\text{O} \left( \frac{\text{at. wt. of H} \times 2}{\text{mol. wt. of H}_2\text{O}} \right) = (1.92) \frac{2}{18} = 0.213$$

$$\left( \frac{\text{wt. of H}}{\text{wt. of sample}} \right) 100 = \left( \frac{0.213}{3.26} \right) 100 = 6.53\% \text{ H}$$

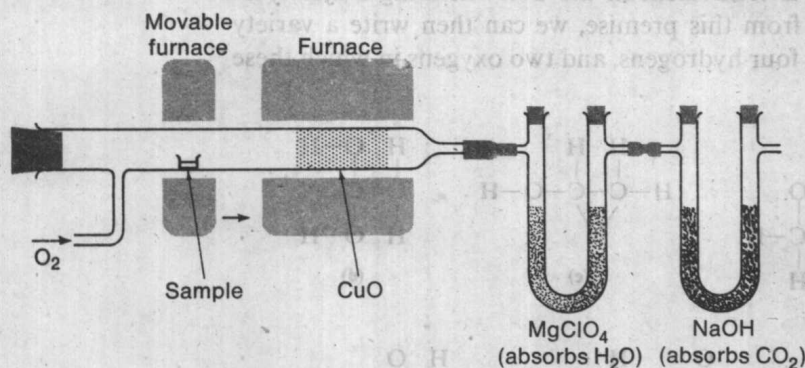
The sum of the percentages of carbon and hydrogen is only 46.13% of the weight of the sample, however, indicating that at least one other element must be present in acetic acid. Since most of the likely possibilities were eliminated by the various qualitative experiments that Berzelius carried out on acetic acid, in which he tested for the presence of halogens, nitrogen, and sulfur, the most probable "other element" is oxygen. Subtracting 46.13% from 100%, then, leaves 53.87% as the oxygen content. Division of each of these percentages by the atomic weight of the element, followed by normalization of these results to the least abundant element present in the compound (i.e., the lowest percent abundance), yields the following figures:

$$39.6/12 = 3.30 \text{ for C} \quad 3.30/3.30 = 1.00 \text{ for C}$$

$$6.53/1 = 6.53 \text{ for H} \quad 6.53/3.30 = 1.98 \text{ for H}$$

$$53.87/16 = 3.36 \text{ for O} \quad 3.36/3.30 = 1.02 \text{ for O}$$

The normalized value for carbon is 1.00, that for hydrogen is 1.98, which is almost 2.00, and that for oxygen is 1.02, which is almost 1.00; this suggests an empirical formula of  $\text{CH}_2\text{O}$ . If the quantitative analysis were absolutely ac-



A recent modification of the combustion analysis dispenses with the weighing tube procedure and simply passes the combustion gases (containing water, carbon dioxide, and other oxides, if other elements are present) through a gas-phase chromatographic unit. The amount of water, carbon dioxide, and other oxides that are present can be read directly from the plot produced by the recorder attached to the instrument.