Organic Chemistry

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Brief Contents

Preface

The inception, formulation, and eventual birth of a new textbook is an evolutionary process, beginning with a need by the author, a need for something better for the students. Upon beginning this project we felt that such a need existed, a text that was better organized and more coherent than currently available texts and written in a style students could both understand and find pleasant. This book is a result of our efforts to attain that goal.

Organic Chemistry is designed and written to be a comprehensive one-year text that can be used with equal facility in courses for chemistry majors, biological science students, and preprofessional students in the medical, dental, and pharmaceutical fields. The text provides a solid background in classical organic chemistry, and the numerous examples of organic compounds of current interest, concern, and/or biochemical importance provide special appeal to the students in the various disciplines.

The text is *written for the student*, in a clear and understandable style, and we made every effort to incorporate detailed explanations of the material so students can use the book on their own. Many published texts assume that students can read between the lines and understand the concepts being put forth; but this is not always true. The real key to studying and learning organic chemistry is a clear and coherent organization. The highlights of the organizational features of this text include:

Functional Group Approach

Organic Chemistry uses the functional group approach, which eliminates the needless repetition and discontinuity of thought that often arises in other texts. For example, we grouped alkanes and cycloalkanes (Chapters 3 and 4), alkenes and alkadienes (Chapters 7 and 8), and atomic and molecular structure (Chapter 2). Also, because the coverage of hydrocarbon chemistry has been reduced, other functional groups (alkyl halides in Chapter 9 and alcohols in Chapter 10) can be easily presented in the first semester. This provides a much more equitable distribution of the material between the two semesters than other texts.

Study Hints

Study hints and other suggestions for study methods that may be potentially useful in helping students succeed and avoid common pitfalls are presented throughout the text. Examples of these highlights, set off by color, include "How To Approach Organic Synthesis," "How To Study Organic Chemistry," "Flash Cards in Organic Chemistry," "How To Draw Resonance Structures," Oxida-

tion and Reduction in Organic Chemistry," "Reactive Intermediates," and "Electrophiles and Nucleophiles." A complete list appears in the Contents of the Study Guide.

Atomic and Molecular Structure

Atomic and molecular structure and molecular orbital theory are presented together in Chapter 2, and the various hybridizations of carbon are developed simultaneously in that chapter. The similarities and differences among these topics can thus be contrasted more readily, to avoid repetition and review in future chapters. For those instructors who choose not to discuss molecular orbital theory, we have separated the theory from the more qualitative discussions of bonding in Chapter 2. Thus, either the qualitative or/and the more theoretical approach to bonding can be taught since they appear in separate sections in the chapter.

Hydrocarbon Chemistry

Numerous modern texts dwell on hydrocarbon chemistry, often to the extent that the first-semester course seldom covers much beyond aromatic chemistry. We reduced the coverage of alkane chemistry, but we still hit the important highlights and introduce the basic concepts that evolve from them. This allows for the coverage of other functional groups, such as alkyl halides (Chapter 9) and alcohols (Chapter 10) in the first semester, permits greater flexibility in the second semester, and gives a better foundation for the laboratory portion of the course.

Mechanisms and Reactive Intermediates

Reaction theory and reaction mechanisms are first introduced and discussed together in Chapter 5, Reaction Mechanisms; nucleophilic aliphatic substitution is also introduced there. Product distribution, the effect of temperature and concentration, the use of stereochemistry, kinetics and isotope labels, and other experimental tools are discussed from the standpoint of explaining how reaction mechanisms are elucidated. The structure of carbocations, carbanions, carbon radicals, and carbenes are all presented in Chapter 2, and in Chapter 5 their relative stabilities, methods of formation, and reactions are contrasted. This material provides a strong foundation for the use of reaction mechanisms throughout the remainder of the text.

Spectroscopy

The spectroscopy material is presented in three separate chapters. Chapter 12 covers infrared and ultraviolet spectroscopy and follows the chapters on alkanes, alkenes, and alkynes; Chapter 15 covers nuclear magnetic resonance and follows aromatic chemistry; and Chapter 18 covers mass spectrometry and follows the aryl halides and phenols. This spreads out the material and gives students time to think about and use their newly gained knowledge of spectral techniques before delving into another technique. Once introduced, spectroscopy is integrated throughout all the subsequent chapters. This building-block ap-

proach provides a sound background in both the understanding and use of spectral methods.

Relevant Examples

Numerous relevant examples of organic compounds of bioorganic, medicinal, industrial, and environmental interest abound throughout the text, including sections on sweeteners, smog, soaps and detergents, natural products, prostaglandins, paints, and polymers. Complete chapters dealing with proteins (Chapter 28) and carbohydrates (Chapter 29) are also included. All these examples are grouped by area and listed in the Contents of the Study Guide.

Summaries

Many summaries of important material are included to help the student, such as summaries of K_a's, K_b's, spectral data, nomenclature, and bond energies. A summary of reactions follows each chapter; a complete reaction summary is compiled in the Study Guide.

Study Problems and Reading References

The text contains more than 900 problems of varying difficulty with over 3000 parts. About 50 percent of these problems are incorporated into the text as questions; about 50 percent are end-of-chapter study questions. Unlike most of the other texts in this field, this text's problems are written for the students—they are the type of problems instructors write for their own exams—and will provide a great deal of needed and useful practice. Reading references are presented in the appendix. Most of these references are from the *Journal of Chemical Education* and can be read and understood by the beginning student; selected textbooks are also listed whenever appropriate.

Study Guide and Answer Book

The Study Guide contains (1) a detailed answer for each problem, (2) a complete summary of nomenclature, (3) a complete summary of all reactions in the text, and (4) lists of relevant sections from the text by area (for example, industrial chemistry, bioorganic chemistry, medicinal chemistry, and environmental chemistry). The Study Guide will be very useful and invaluable to students as an aid in understanding and mastering organic chemistry.

Acknowledgments

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Our typists, Betty Caret, Kathy Mulqueen, Sharon Osenburg, and Nancy Scales, who made it all possible, deserve much credit.

And finally, we express our indebtedness to our students who gave us the reason for beginning, the courage to continue, and the fortitude to complete the project.

We are sincerely grateful to them all.

Alan S. Wingrove
Robert L. Caret

Organic Chemistry

PERIODIC TABLE OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H 1.00797																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.944
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.60	33 As 74.922	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	57 *La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.20	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 †Ac (227)	104 Ku (261)	105 Ha (260)													

58 *Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

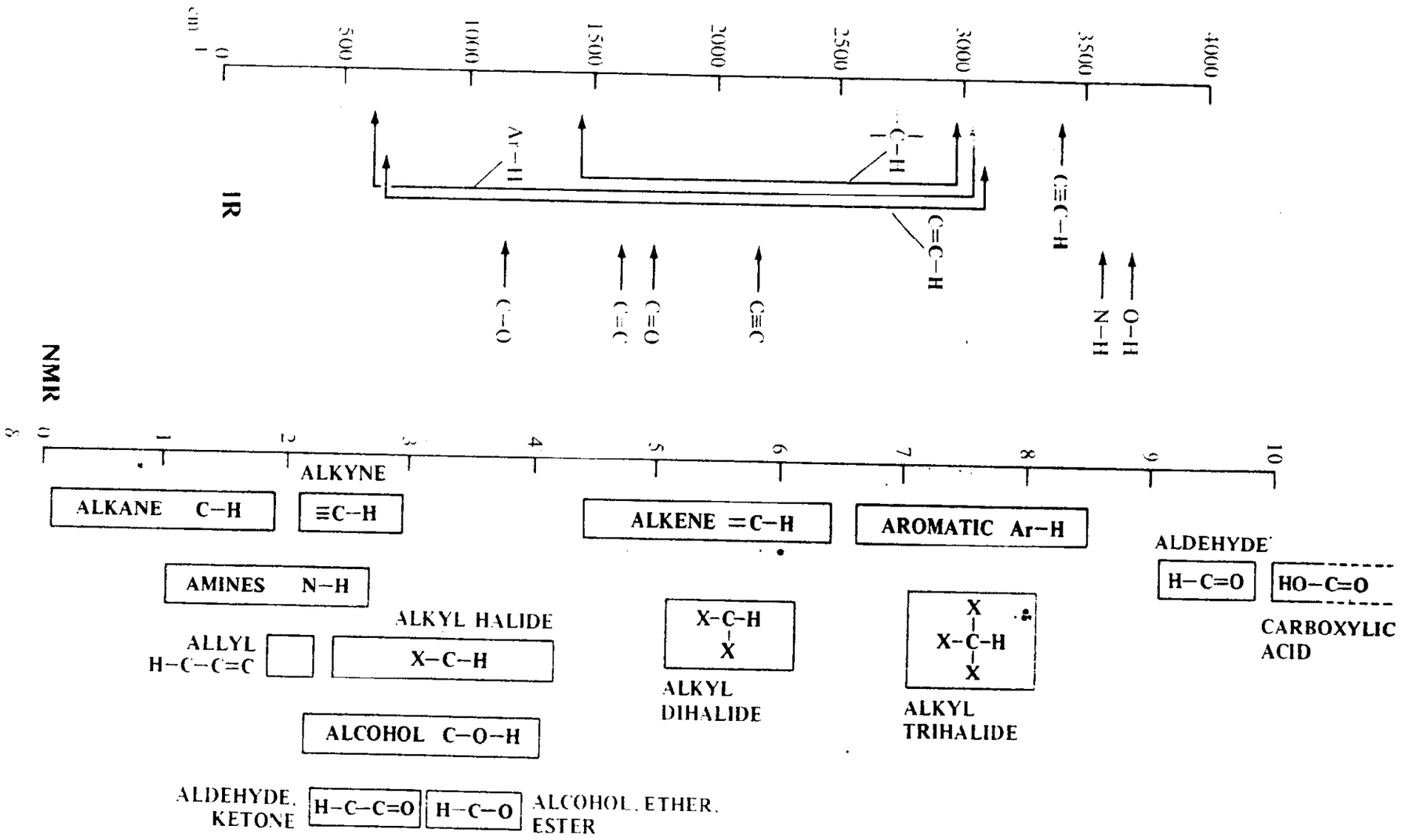
90 †Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lw (257)

MULTIPLE ATOMIC WEIGHTS OF THE ELEMENTS

C_1	12.01	H_1	1.01	O_1	16.00
C_2	24.02	H_2	2.02	O_2	32.00
C_3	36.03	H_3	3.02	O_3	48.00
C_4	48.04	H_4	4.03	O_4	64.00
C_5	60.06	H_5	5.04	O_5	79.99
C_6	72.07	H_6	6.05	O_6	95.99
C_7	84.08	H_7	7.06	O_7	111.99
C_8	96.08	H_8	8.06	O_8	127.99
C_9	108.10	H_9	9.07	O_9	143.99
C_{10}	120.11	H_{10}	10.08	O_{10}	159.98

N_1	14.01	F_1	19.00	Cl_1	35.45
N_2	28.01	F_2	38.00	Cl_2	70.91
N_3	42.02	F_3	57.00	Cl_3	106.36
N_4	56.03	F_4	75.99	Cl_4	141.81
N_5	70.03	F_5	94.99	Cl_5	177.27

Br_1	79.91	I_1	126.90
Br_2	159.83	I_2	253.81
Br_3	239.75	I_3	380.71
Br_4	319.66	I_4	507.62
Br_5	399.58	I_5	634.52


cm⁻¹
0
500
1000
1500
2000
2500
3000
3500
4000
IR
Ar–H
C–H
C≡C–H
C=C–H
C–O
C=C
C=O
C≡C
N–H
O–H
NMR
δ
0
1
2
3
4
5
6
7
8
9
10
ALKYNE
ALKANE C–H
≡C–H
ALKENE =C–H
AROMATIC Ar–H
ALDEHYDE
H–C=O
HO–C=O
CARBOXYLIC ACID
AMINES N–H
ALKYL HALIDE
ALLYL
H–C–C=C
X–C–H
X–C–H
X
ALKYL DIHALIDE
X
X–C–H
X
ALKYL TRIHALIDE
ALCOHOL C–O–H
ALDEHYDE, KETONE
H–C–C=O
H–C–O
ALCOHOL, ETHER, ESTER

QUICK REFERENCES

NOMENCLATURE

Alkanes	Sec. 3.10
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Alcohols	10.1
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Ethers	19.1
Carboxylic Acids	22.1
Acid Derivatives	23.1
Aldehydes	20.2
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K_a's, K_b's

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Alcohols	10.9
Phenols	17.4, 17.5
Carboxylic Acids	22.9
Amines	26.3, 26.5B
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BOND DISSOCIATION ENERGIES

Table 5-1

Detailed Contents