

Jane M. Cram and Donald J. Cram

The Essence of
Organic
Chemistry

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University of California, Los Angeles

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The Essence of Organic

Preface

No authors write a new textbook of elementary organic chemistry without the belief that they can improve on the many already available. We are no exception. Our major challenge in developing this book was to encompass the main themes of organic chemistry in the space of 500 pages. A second challenge was to develop a text which was as little dependent on the teacher and on ancillary material as possible. A third challenge has been to introduce enough biological chemistry to illustrate the analogies and dissimilarities between the compounds and reactions found in the laboratory and in the cell. Although the students to whom this book is addressed have different career objectives, enough of them are oriented toward the life sciences to justify our stress of those features of organic chemistry most relevant to life processes.

The enormous correlative power of the structural theory of organic chemistry finds its expression in the classes of organic compounds on the one hand, and the classes of organic reactions on the other. The organization of the text at the chapter level follows the traditional pattern in which compound classes are taken up in order of their increasing complexity. The first four chapters deal largely with the nature of the chemical bond as applied to the structures, reactions, and physical properties of hydrocarbons. In these chapters, the other classes of compounds are introduced as derivatives of the hydrocarbons and of simple inorganic compounds already familiar to the student. Chapter 5 treats alcohols, phenols, and ethers, which are the simple organic derivatives of water. Chapter 6 introduces the alkyl halides, sulfates, phosphates, thiols, and sulfides, which are organic derivatives of the simple inorganic acids. The compound classes treated through Chapter 6 can be interconverted largely through simple substitution, addition, and elimination reactions. Thus the reaction classes with their similar general mechanistic features are used to integrate otherwise individual reactions into families of reactions.

By the time Chapter 7 is reached, enough compounds and reactions have been discussed to allow a thorough treatment of chirality and of dynamic stereochemistry. Once developed, the stereochemical themes appear again and again in the subsequent discussions. Chapters 8 and 9 deal with carboxylic acids and their near relatives, the acid chlorides, esters, and fats. These compounds and their interconvertibility provide analogies for the amines, amides, and proteins of Chapter 10. In Chapter 11 on aldehydes and ketones, oxidation, reduction, and condensation

Preface

reactions relate these compounds to those compound classes discussed previously. These middle chapters provide opportunities for comparing and contrasting the structures and reactions of organic and biochemistry. While the facts and theories of organic chemistry build on one another as the book progresses, the biochemical sections depend directly on the preceding organic sections rather than on preceding biochemical sections.

Chapters 12 through 15 in turn take up aromatic substitution, carbohydrates, carbon chain-building reactions, and organic spectroscopy. The unique character of each of these subjects and the absence of their interdependence allows them to be studied in any order.

In our attempt to make this book as self-contained as possible, subjects are not mentioned unless they are treated in depth. Problems are interspersed with the text so the students can test their knowledge section by section. The problems at the end of each chapter depend more on the chapter taken as a whole and on material found in previous chapters. The problems become progressively more difficult as the end of the problem section is approached. So that the students can learn whether they have been successful in answering our problems, *the answers to all problems are found at the end of the book*. The important topics and reactions summarized at the end of each chapter provide the students with an overview of the subject.

A separate Study Guide for Students has been written to help them learn the material in this text. The text and the Study Guide play reciprocal roles, not unlike those of participants in a dialogue. Thus the Study Guide poses a series of questions to which the continuity of the text provides the series of answers. Conversely, the Study Guide reveals the thought patterns required for solutions of the more difficult problems in the text. The questions of the Study Guide are Socratic in character and anticipate the development of the subject matter in the text. The questions of the text are designed to allow the students to measure their progress and to self-test their development.

We are indebted to Professor J. John Uebel of the University of New Hampshire and to Professor Kenneth G. Hancock of the University of California at Davis, who read the entire manuscript, for their many constructive comments and suggestions. The comments of a number of reviewers helped to shape the book in its early stages. It has been a pleasure to work with Miss Laura Rich, the editor, whose consistent

Contents

Chapter 1 The Ingredients of Organic Compounds: Atoms, Orbitals

interest helped to move the book through to completion. Lastly, we wish to acknowledge the impatience and lack of cooperation between the coauthors, without which this book would never have been completed.

Los Angeles, California
September 1977

J. M. C.
D. J. C.

Chapter 2 Structural Theory Applied to Saturated Hydrocarbons and Their Derivatives

2.1 Hydrocarbons Similar to Methane	25
2.2 Structural Isomers	29
2.3 Systematic Nomenclature for Alkanes—IUPAC	30
2.4 Conformations of Large Molecules	31
2.5 Sources and Uses of Alkanes	34
2.6 Simple Names for Small Alkyl Groups	35
2.7 Structural Isomerism in Derivatives of Alkanes	36
2.8 Cyclic Hydrocarbons	40
2.9 Isomerism in Cyclic Compounds	41
2.10 Conformations of Cyclohexane	43

Chapter 3 Structural Theory Applied to Unsaturated Compounds

3.1 Unsaturated Hydrocarbons—Alkenes and Alkynes	51
3.2 Geometry of Unsaturated Hydrocarbons	53
3.3 Stereoisomerism of Alkenes—Cis-Trans Isomerism	57
3.4 Aromatic Compounds	60
3.5 Carbonyl and Quaternary Compounds	62
3.6 Carbons, Oxygen, Double Bonds—Aldehydes and Ketones	63

Contents

Chapter 1 The Ingredients of Organic Compounds: Atoms, Orbitals and Bonds

1.1	Perspective	2
1.2	Carbon Compounds	4
1.3	Electron Structure and Combining Rules for Small Molecules	5
1.4	Shapes of Small Molecules in Three Dimensions	6
1.5	Atomic and Molecular Orbital View of Bonding	8
1.6	The Atomic Orbitals of Carbon	10
1.7	Functional Groups	12
1.8	Classes of Organic Compounds	13
1.9	The Polar Covalent Bond	14
1.10	Polar Compounds	16
1.11	Hydrogen Bonding	17
1.12	Effect of Intermolecular Attractions on Physical Properties	18

Chapter 2 Structural Theory Applied to Saturated Hydrocarbons and Their Derivatives

2.1	Hydrocarbons Similar to Methane	25
2.2	Structural Isomers	29
2.3	Systematic Nomenclature for Alkanes—IUPAC	30
2.4	Conformations of Large Molecules	31
2.5	Sources and Uses of Alkanes	34
2.6	Simple Names for Small Alkyl Groups	36
2.7	Structural Isomerism in Derivatives of Alkanes	38
2.8	Cyclic Hydrocarbons	40
2.9	Isomerism in Cyclic Compounds	41
2.10	Conformations of Cyclohexane	43

Chapter 3 Structural Theory Applied to Unsaturated Compounds

3.1	Unsaturated Hydrocarbons—Alkenes and Alkynes	51
3.2	Geometry of Unsaturated Hydrocarbons	53
3.3	Stereoisomerism of Alkenes— <i>Cis-Trans</i> Isomerism	57
3.4	Aromatic Compounds	60
3.5	Carbonate and Guanidinium Ions	63
3.6	Carbon–Oxygen Double Bonds—Aldehydes and Ketones	65

Contents

3.7	The Carboxylic Acid Family of Compounds	66
3.8	Organic Acids and Bases	68
3.9	A Look at a Large Molecule	72

Chapter 4 Alkenes and Alkynes

4.1	Sources and Uses of Alkenes, Dienes, and Polyenes	79
4.2	Nomenclature of Alkenes	80
4.3	Hydrogenation of Alkenes	84
4.4	Addition of Polar Reagents to Alkenes	85
4.5	Orientation in Addition of Unsymmetrical Reagents	88
4.6	Addition of Halogens to Alkenes	90
4.7	Other Addition Reactions of Alkenes	91
4.8	Alkynes	94
4.9	Reactions of Alkynes	95
4.10	Terpenes	97

Chapter 5 Alcohols, Phenols, and Ethers

5.1	Sources and Uses of Alcohols	108
5.2	Nomenclature of Alcohols	111
5.3	Physical Properties of Alcohols	113
5.4	Alcohols as Acids and Bases	113
5.5	Reactions of Alcohols that Cleave the C—O Bond	115
5.6	Dehydration of Alcohols to Alkenes	118
5.7	Methods of Preparation of Alcohols	119
5.8	Phenols	122
5.9	Acidity of Phenols	125
5.10	Ethers	126
5.11	Oxiranes (Epoxides)	127
5.12	Reactions of Oxiranes (Epoxides)	129
5.13	Steroids	130

Chapter 6 Alkyl Halides and Their Relatives

6.1	Sources and Uses of Alkyl Halides	138
6.2	Nomenclature of Alkyl Halides	140
6.3	Reactions of Alkyl Halides—Substitution	141

6.4	Mechanisms of Nucleophilic Substitution and of Elimination	144
6.5	Alkenes from Alkyl Halides	147
6.6	Preparation of Alkyl Halides	149
6.7	Alcohol Derivatives—Esters of Sulfonic and Phosphoric Acids	149
6.8	Substitution in the Biosynthesis of Terpenes	153
6.9	Thiols, Sulfides, and Disulfides	154
6.10	Biological Transmethylation Reactions	157
Chapter 7 Shells, Shoes, Screws, and Chiral Molecules		
7.1	Shells, Shoes, and Screws	166
7.2	The Plane of Symmetry	168
7.3	A Review of the Types of Isomerism	169
7.4	Enantiomers	171
7.5	Optical Activity	173
7.6	Absolute Configuration and Notation	175
7.7	Racemic Forms	177
7.8	Diastereoisomers	178
7.9	Resolution of Racemic Forms	179
7.10	Meso Forms	180
7.11	Dynamic Stereochemistry	183
7.12	Stereochemistry of Nucleophilic Substitution	185
7.13	Stereochemistry of Elimination Initiated by Base	187
Chapter 8 Carboxylic Acids and Acyl Chlorides		
8.1	Sources and Uses of Carboxylic Acids	194
8.2	The Carboxyl Functional Group	195
8.3	Nomenclature of Carboxylic Acids	197
8.4	Physical Properties of Carboxylic Acids	200
8.5	Hydrogen Bonding	201
8.6	Salt Formation of Carboxylic Acids	202
8.7	The Acidity of Carboxylic Acids	202
8.8	Effect of Structure on Acidity of Carboxylic Acids	204
8.9	Conversion of Carboxylic Acids to Acid Chlorides	205
8.10	Methods of Synthesis of Carboxylic Acids	206
8.11	Greek-Letter Notation and Nomenclature	208

8.12	Hydroxyacids	208
8.13	Prostaglandins	209
8.14	Acid Chlorides	210
8.15	Nomenclature of Acid Chlorides	211
8.16	Reactions of Acid Chlorides to Form Esters	211
8.17	Mechanism of the Substitution Reactions of Acid Chlorides and Other Acid Derivatives	213
8.18	Reactions of Acid Chlorides to Form Amides	215
8.19	Other Substitution Reactions of Acyl Chlorides	217
8.20	Dicarboxylic Acids	218
8.21	Carboxylic Acid Anhydrides	220
Chapter 9 Esters and Fats		
9.1	Sources and Uses of Esters	229
9.2	The Ester Group	230
9.3	Nomenclature of Esters	231
9.4	Hydrolysis of Esters by Bases	232
9.5	Transesterification	234
9.6	Esters to Amides	234
9.7	Esters to Alcohols—Reduction by Lithium Aluminum Hydride	235
9.8	Thioesters	236
9.9	Reactions of Thioesters	236
9.10	Relative Reactivity of Carboxyl Functional Groups	238
9.11	Acid-Catalyzed Hydrolysis of Esters and Esterification of Acids	238
9.12	The Nature of Catalysis	239
9.13	Fats and Phospholipids	241
9.14	Soaps, Detergents, and Other Emulsifiers	245
9.15	Models of Biological Phosphate Compounds	250
9.16	Biological Ester Formation	251
Chapter 10 Amines, Amides, and Proteins		
10.1	Sources and Uses of Amines	260
10.2	Nomenclature of Amines	262
10.3	Physical Properties of Amines	264
10.4	Amines as Organic Bases	265

10.5	Reactions of Amines that Form a New C—N Bond	267
10.6	Preparation of Amines	269
10.7	Sources and Uses of Amides	271
10.8	Nomenclature of Amides	272
10.9	The Amide Functional Group	273
10.10	Acidity and Basicity of Amides	275
10.11	Hydrolysis of Amides	275
10.12	Preparation of Amides	276
10.13	Amino Acids	277
10.14	α -Amino Acids—Protein Building Blocks	278
10.15	Proteins	281
10.16	Determination of an Amino Acid Sequence of Protein	283
10.17	Chemical Synthesis of Proteins	286
10.18	The Work of an Enzyme: Chymotrypsin Catalysis of Amide Hydrolysis	288
10.19	Structural Organization of Proteins	292

Chapter 11 Aldehydes and Ketones

11.1	Sources and Uses of Aldehydes and Ketones	302
11.2	The Carbonyl Functional Group	303
11.3	Nomenclature of Aldehydes and Ketones	305
11.4	Mechanism of Reactions of Carbonyl Compounds	308
11.5	Addition of Water and Alcohol to Carbonyl Compounds	309
11.6	Reaction of Carbonyl Compounds with Ammonia and Amines	312
11.7	Addition of Hydrogen Cyanide—Formation of a New Carbon-Carbon Bond	314
11.8	Reactions of Carbonyl Compounds that Involve the Hydrogen on the α -Carbon	317
11.9	Keto-Enol Equilibria	318
11.10	The Aldol Condensation Reaction	320
11.11	Oxidation and Reduction of Carbonyl Compounds	322
11.12	Methods of Preparation of Aldehydes and Ketones	324
11.13	Biological Oxidation-Reduction System that Interconverts Carbonyl- and Hydroxyl-Containing Compounds	326
11.14	Reactions of Imines of Pyridoxal and Amino Acids	327

Chapter 12 Reactions of Aromatic Rings

12.1 The Benzene Story—Aromaticity	340
12.2 Sources and Uses of Aromatic Compounds	344
12.3 Delocalization Energy of Benzene	346
12.4 General Mechanism of Electrophilic Aromatic Substitution	347
12.5 Nitration	347
12.6 Bromination	349
12.7 Friedel-Crafts Alkylation and Acylation	350
12.8 Sulfonation	352
12.9 Orientation in Substitution of Benzene Derivatives	354
12.10 Diazonium Ions	357
12.11 Dyes and Pigments	359
12.12 Aryl Halides—Nucleophilic Aromatic Substitution	361

Chapter 13 Carbohydrates and Sugar-Containing Compounds

13.1 Carbohydrates	370
13.2 Monosaccharides	371
13.3 Diastereoisomers of Monosaccharides	372
13.4 Hemiacetals and Acetals of Glucose—Glucosides	376
13.5 Other Reactions of Monosaccharides	379
13.6 Biosynthesis of Glucose by an Aldol Condensation of Trioses	380
13.7 Disaccharides	382
13.8 Polysaccharides	383
13.9 N-Glycosides of D-Ribose in the Structures of Coenzymes	385
13.10 Polynucleotides—The Nucleic Acids, DNA and RNA	389
13.11 Transfer RNA as a Reactant in the Biosynthesis of a Polypeptide	391
13.12 The Double Helix of DNA	394

Chapter 14 Carbon Chain-Building Reactions

14.1 Organometallic Compounds	402
14.2 Grignard Reagents from Alkyl and Aryl Halides	404
14.3 Reactions of Grignard Reagents with Carbonyl Compounds	406
14.4 Reactions of Grignard Reagents with Esters	408
14.5 Sodium Enolate Salts	410
14.6 The Aldol Condensation	412

CHAPTER 1

14.7	The Claisen Ester Condensation and the Reverse Reactions	413
14.8	Enzyme-Catalyzed Claisen Condensations in Biosynthesis	415
14.9	Degradation of Fatty Acids by Cleavage of a β -Ketoester	417
14.10	Malonic Ester Reactions and Decarboxylations	419
14.11	Malonic Acid in Biosynthesis	421
14.12	The Citric Acid Cycle	422
14.13	Vinyl Polymerization	424

Chapter 15 Spectroscopy of Organic Compounds

15.1	Spectroscopy and Molecular Structure	436
15.2	The Ultraviolet-Visible Spectrum	438
15.3	The Infrared Spectrum	440
15.4	The Nuclear Magnetic Resonance Spectrum	442
15.5	Number of Signals in the NMR	443
15.6	The Position of NMR Signals: The Chemical Shift	444
15.7	Intensity of the Signal: The Number of Protons	446
15.8	Signal Splitting: The Number of Neighboring Protons	446
15.9	Spectra of Hydrocarbons	448
15.10	Spectra of Alcohols, Ethers, Alkyl Halides, and Amines	450
15.11	Spectra of the Carboxylic Acid Family and of Aldehydes and Ketones	452

Answers to Problems	A-1
----------------------------	------------

Index	I-1
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CHAPTER 1

The Ingredients of Organic Compounds: Atoms, Orbitals, and Bonds

Human beings are curious; otherwise the questions that organic chemistry answers would never have been asked. These questions originally centered around attempts to understand life processes and the operations of "organs," hence the term **organic chemistry**. Since compounds of carbon and hydrogen were always encountered in organs, organic chemistry became associated with the study of compounds of carbon and hydrogen. As the science developed, many compounds of carbon and hydrogen were synthesized in the laboratory which were identical to those isolated from "organic" sources. Many others were prepared that were unrelated to the *natural* compounds. Some of the syntheses involved inorganic starting materials, but most were transformations of one compound of carbon and hydrogen into a second, a third, etc. Since the properties of the compounds were found to be independent of their "natural" or "unnatural" origins, the term organic chemistry became more general, and now refers to the **chemistry of compounds that contain carbon and hydrogen**.

The intimate relationship between laboratory and cellular chemistry continues, and the term "organic" appropriately refers to that relationship. The evolutionary compounds of carbon produced in cells and those compounds prepared in the laboratory are governed by the same chemical rules. This book, then, describes the compounds of carbon and hydrogen and the rules that govern their transformations.

1.1 PERSPECTIVE

Matter exhibits different organizational characteristics at different temperatures. Above about 100,000°K, the electrons and nuclei that compose plasma are stable and associate to form atoms only below that temperature. Atoms, in turn, associate to form molecules only at temperatures below a few thousand degrees. The common chemical bonds of organic compounds are those between carbon and carbon, carbon and hydrogen, carbon and oxygen, carbon and nitrogen, carbon and sulfur, and carbon and the halogens. These bonds are stable only in the range between absolute zero and about 1000°K. Evolutionary organic compounds, those associated with living systems, are produced and used at temperatures that vary between about 260°K and 373°K, and are often unstable at higher temperatures. "Unnatural" organic compounds have been designed and synthesized which are stable to about 773°K, but these are noteworthy exceptions, since most organic compounds decompose at much lower temperatures.

What are the sizes of organic compounds? One of the smallest molecules is methane (the main component in natural gas), which is about 0.0000003 cm in diameter. One of the largest is polyethylene, which can be as long as 0.00009 cm. A small enzyme molecule—one of the machines of life—is about 0.000003 cm in diameter. The size of objects in the world we perceive with the unaided eye ranges from 10^{-2} to 10^{10} cm (0.01 to 10 billion cm). Even with the help of the electron microscope, our sight can barely detect only the largest organic compounds,