

# Introduction to Organic Chemistry

*SECOND EDITION*

Andrew Streitwieser, Jr.  
Clayton H. Heathcock

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**Andrew  
Clayton H. Heathcock**

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# A Note to the Student

BEFORE you begin your adventure in organic chemistry it is perhaps appropriate for you to take a few minutes to plan your journey. The first chapter of this book provides a succinct history of the development of chemical science up to the beginnings of organic chemistry in the middle of the last century. Immediately following is a brief review of the important concepts of orbitals and chemical bonds. Although Chapter 2 is a review of topics you learned in your general chemistry course, it is essential that you be familiar with this material before proceeding with your study. Therefore, take an hour or so to go over this chapter and work the problems, even if your instructor does not specifically repeat the review material in lecture.

Chapters 3 and 4 are intended to introduce you to the two important aspects of organic chemistry—structures and reactions. Although some general chemistry courses will have covered the subject matter of these two chapters, many will not. Again, you should be thoroughly acquainted with the material in Chapters 3 and 4 before going further with your studies.

In Chapter 5 you will encounter the simplest organic compounds, those made up solely of carbon and hydrogen. This chapter also introduces two basic principles—thermodynamics and conformations. In Chapter 6 you will find the first detailed study of an organic reaction, free radical halogenation, and you will be able to put into practice the general ideas of reaction mechanisms and thermodynamics presented in Chapters 4 and 5. Chapter 7 will introduce you to a fascinating topic—stereochemistry. This special aspect of molecular structure is of fundamental importance to organic chemistry and to biochemistry. Although you may find thinking in three dimensions difficult at first, practice pays off. Once you can freely visualize organic compounds as three-dimensional objects just like the familiar objects of your everyday life, you will discover that organic chemistry is suddenly “much easier” than you thought.

The displacement reaction mechanism, which is treated in Chapter 8, is one of the fundamental mechanisms of organic chemistry. It is important that you grasp the generality of this mechanism because you will find that the same relationships of structure to reactivity recur over and over again in organic chemistry. By acquiring an early understanding of the principles of the displacement reaction, you can avoid mindlessly memorizing dozens of reactions; you will be able to recognize that many “new” reactions are only different versions of reactions you already understand.

At Chapter 9 you will shift gears and turn from chemical reactivity back to chemical structure. In this chapter you will have your first encounter with spectroscopy, which is the way organic chemists find out how the atoms of a molecule are joined together. In all, four chapters of the book are devoted to various forms of spectroscopy—Chapter 9 (nuclear magnetic resonance spectroscopy), Chapter 14 (infrared spectroscopy), Chapter 17 (mass spectrometry), and Chapter 21 (ultraviolet spectroscopy). Each kind of spectroscopy gives us different pieces of the molecular jigsaw puzzle, but nuclear magnetic resonance spectroscopy is the most important.

As you progress in your study of organic chemistry, you will discover that the

science is conveniently organized in terms of *functional groups*—the parts of organic compounds other than the carbon-carbon and carbon-hydrogen single bonds that are common to all organic structures. Several chapters systematically treat the chemistry of various functional group classes of organic compounds—alcohols and ethers (Chapter 10), alkenes (Chapter 11), alkynes (Chapter 12), aldehydes and ketones (Chapter 13), organometallic compounds (Chapter 15), carboxylic acids (Chapter 18), and derivatives of carboxylic acids (Chapter 19). In each of these chapters the topical sequence is similar.

1. The functional group itself—its characteristic geometry and its effect on the geometry of the hydrocarbon part of the molecule containing it.
2. How compounds of the class are named.
3. The common physical properties of the class of compounds under consideration, including characteristic spectral properties.
4. The chemical reactions that are characteristic of the functional group, to which the bulk of the chapter is devoted.

In most organic reactions one functional group is typically transformed into another. Thus, you will find that an organic reaction can usually be thought of both as a characteristic of a given class of compounds and as a characteristic method of preparation of another class of compounds. In this book you will find that reactions are generally introduced as a characteristic property of a class of compounds. However, each functional group chapter also contains a section on preparative methods. In general, the emphasis in these preparation sections is on the practical aspects of the reactions rather than on the mechanistic aspects.

Chapter 16 is rather different from the other chapters in the book in that it is essentially a review of the organic chemistry learned up to that point. In some ways, learning organic chemistry is like learning a language. The simple reactions and mechanistic principles are like the vocabulary of the language. As in learning a language, you must first learn the vocabulary. However, if you only know the words of a language you will not be able to compose a poem, or even rent a hotel room with hot and cold running water. It is necessary also to learn how the words are put together to make sentences—the grammar and syntax of the language. In organic chemistry we learn to put several simple reactions together to achieve an overall transformation that cannot be accomplished by any single reaction. Chapter 16 will give you an opportunity to practice multistep synthesis using the reactions you have learned.

In the first half of the book, you will consider the typical chemical properties of molecules having a single functional group. In Chapter 20 you will discover that compounds having two functional groups can have properties that are very different from those of compounds having only one of the groups. This study of “conjugated systems” is fundamental to the study of ultraviolet spectroscopy (Chapter 21) and aromatic chemistry (Chapters 22 and 23). The remainder of the book contains a good deal of chemistry of such “polyfunctional” compounds. For example, Chapter 27 treats the special chemistry of compounds with two oxygen-containing functional groups. Chapters 28 and 29 cover the chemistry of two important families of polyfunctional “natural products”—carbohydrates and amino acids.

Up to Chapter 24 your study of organic chemistry will have dealt with compounds made up mainly of carbon, hydrogen, oxygen, and the halogens. In Chapters 24–26 you will encounter organic compounds of nitrogen, phosphorus, and sulfur. Of these compounds, the amines (Chapter 24) are the most important, but the other nitrogen functions (Chapter 25) are also important, especially in aro-

matic chemistry. Although your instructor may choose to omit Chapter 26 (sulfur and phosphorus compounds), if you are bound for a career in medicine or in the health sciences, you will want at least to read through this chapter.

Chapters 30–32 deal with further aspects of aromatic chemistry. The astute student will recognize that there are virtually no new concepts in these three chapters, rather, they serve to add flesh to the bones of the subject. However, it is interesting flesh, and the future chemical engineer or physician will find in these chapters many hints of things to come.

The final two chapters of the book are optional reading. Chapter 33 is an introduction to the literature of chemistry. Although you may not need to use the chemical literature at this point in your career, many of you will need this knowledge later. Chapter 33 will give you a start at the appropriate time. Chapter 34 is a collection of brief essays on topics somewhat beyond the scope of a general introduction. These essays are provided to give the interested student a glimpse of some of the exciting areas of modern research.

It is also appropriate at this point to mention several tools we have provided to assist you in learning organic chemistry. The first is the “indented sections,” which are in smaller type and, as a further aid to their recognition, are set apart by brackets at the left and right. These sections, which are found at various points within each chapter, contain several types of information. Some give more detailed information on the topic immediately preceding. Others contain specific reaction conditions for a reaction that has been used for an example. Still others convey information of interest about specific compounds, often inorganic compounds that are employed as reagents in organic chemistry. These indented sections are set apart so that they may be skipped over by the student who is just reviewing the important principles of the chapter. Our rule of thumb at Berkeley is that the material in these sections is for enrichment, and that students are not held responsible for it on examinations. You should ask your instructor about the policy in your course.

A second invaluable tool is the exercises and problems in each chapter. The exercises, which are at the ends of most sections, are cast mainly in the form of “drill” to provide you with immediate practice in using new principles or reactions you have just learned. For many of you, these exercises will seem ridiculously easy, as you will be asked to write out an equation you have just learned. However, they are an important part of the learning process. Everyone has had the experience of “daydreaming” while reading merrily along. It is possible to read several pages and be totally unconscious of what you have read. The exercises force you to pause periodically and check to see that you have really been assimilating what you have been reading. The problems at the end of each chapter also contain some drill questions, but the parts of a single question may draw from many different sections of the chapter. Thus, these questions provide for a second check on your retention of the various reactions and principles you have studied. There are also “thought questions” that ask you to take several reactions or principles and put them together to solve a problem or in some cases to extend your knowledge and discover something for yourself.

To enable you to derive the greatest benefit from the exercises and problems, we have prepared a Student Study Guide. This paperback book contains worked-out answers to all of the exercises and problems as well as a key-word index and study hints for each chapter. In addition, the study guide contains supplemental problems, with answers. It is important that you give any problem a good try before looking up the answer. It is human nature to quit worrying about a problem as soon as the answer is known, and it is also true that we learn more

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**A Note to the  
Student**

from a problem we have labored over than from one we haven't given much thought to.

One teaching device we have used requires special mention—the three dimensional stereoscopic projections that are distributed throughout the book (see list, page xvii). These computer-generated images are designed so that you may see the figure in three dimensions. By using a suitable viewer one may cause each eye to focus independently on one of the two images of such a projection, and there is an illusion of depth to the resulting picture one sees. An inexpensive cardboard viewer is available from the Taylor-Merchant Corporation, 25 West 45 Street, New York, NY 10036. Most bookstores will not stock these viewers unless the Professor in a course requests it. If your bookstore does not have a supply of viewers, ask that they be ordered. It is actually possible, albeit a bit more difficult, to see a stereo image without the special viewer. To do this, hold the page about 20 inches from your eyes and focus on a point behind the book in such a way that the two images merge. Generally, the merged image will suddenly seem three-dimensional. One caution with this method the right eye will sometimes focus on the left image and vice versa. The result is the perception of the mirror image, a concern when precise stereochemistry is important, as in Chapter 7.

With these general suggestions in mind, it remains only for us to wish you luck as you set out upon your journey through organic chemistry. Both of us look back with fond remembrance upon our own discovery of this fascinating subject, we hope that you will find it as rewarding.

ANDREW STREITWIESER, JR  
CLAYTON H. HEATHCOCK

# Contents

<b>1. Introduction</b>	<b>1</b>
<b>2. Electronic Structure and Bonding</b>	<b>5</b>
2.1 Periodic Table	5
2.2 Lewis Structures	5
2.3 Geometric Structure	9
2.4 Resonance Structure	10
2.5 Atomic Orbitals	15
2.6 Electronic Structure of Atoms	18
2.7 Bonds and Overlap	19
2.8 Hybrid Orbitals and Bonds	22
PROBLEMS	26
<b>3. Organic Structures</b>	<b>29</b>
3.1 Introduction	29
3.2 The Shape of Molecules	32
3.3 Functional Groups	33
3.4 The Determination of Organic Structures	37
3.5 <i>n</i> -Alkanes, the Simplest Organic Compounds	40
3.6 Systematic Nomenclature	42
PROBLEMS	47
<b>4. Organic Reactions</b>	<b>51</b>
4.1 Introduction	51
4.2 An Example of an Organic Reaction: Equilibria	51
4.3 Reaction Kinetics	53
4.4 Reaction Profiles and Mechanism	55
4.5 Acidity and Basicity	60
PROBLEMS	65
<b>5. Alkanes</b>	<b>69</b>
5.1 <i>n</i> -Alkanes: Physical Properties	69
5.2 <i>n</i> -Alkanes: Barriers to Rotation	71
5.3 Branched-Chain Alkanes	76
5.4 Cycloalkanes	78
5.5 Heats of Formation	80
5.6 Cycloalkanes: Ring Strain	82
5.7 Cycloalkanes: Conformation	83
5.8 Substituted Cyclohexanes	90
5.9 Occurrence of Alkanes	95
PROBLEMS	97
<b>6. Reactions of Alkanes</b>	<b>100</b>
6.1 Bond-Dissociation Energies	100
6.2 Pyrolysis of Alkanes: Cracking	103



6 3	Halogenation of Alkanes	104
6 4	Combustion of Alkanes	115
6 5	Average Bond Energies	118
	PROBLEMS	118
<b>7.</b>	<b>Stereoisomerism</b>	122
7 1	Chirality and Enantiomers	122
7 2	Physical Properties of Enantiomers Optical Activity	124
7 3	Nomenclature of Enantiomers The R,S Convention	127
7 4	Racemic Mixtures	131
7 5	Fischer Projections	132
7 6	Compounds Containing More Than One Asymmetric Atom; Diastereomers	134
7 7	Stereoisomeric Relationship in Cyclic Compounds	137
7 8	Chemical Reactions and Stereoisomerism	139
	PROBLEMS	143
<b>8.</b>	<b>Alkyl Halides; Nucleophilic Substitution and Elimination</b>	147
8 1	Structure	147
8.2	Physical Properties	149
8.3	Conformations	151
8 4	Some Uses of Halogenated Hydrocarbons	152
8.5	The Displacement Reaction	154
8 6	Stereochemistry of the Displacement Reaction	156
8 7	Generality of the Displacement Reaction	160
8 8	Effect of Substrate Structure on Displacement Reactions	161
8 9	Nucleophilicity and Solvent Effects	164
8 10	Leaving Groups	169
8 11	E2 Elimination	171
8 12	S <sub>N</sub> 1 Reactions Carbocations	173
8 13	Summation Elimination Versus Substitution. Unimolecular Versus Bimolecular	178
8.14	Ring Systems	179
	PROBLEMS	181
<b>9.</b>	<b>Nuclear Magnetic Resonance Spectroscopy</b>	186
9.1	Structure Determination	186
9 2	Introduction to Spectroscopy	187
9.3	Nuclear Magnetic Resonance	188
9.4	Chemical Shift	191
9 5	Relative Peak Areas	195
9.6	Spin-Spin Splitting	197
9 7	More Complex Splitting	205
9.8	Solving Spectral Problems	208
9 9	Nmr Spectroscopy of Other Nuclei	210
9 10	Dynamical Systems	216
	PROBLEMS	218
<b>10.</b>	<b>Alcohols and Ethers</b>	229
10 1	Introduction Structure	229
10 2	Nomenclature of Alcohols	230
10 3	Physical Properties of Alcohols	233

10 4	Acidity of Alcohols Inductive Effects	237
10 5	Nuclear Magnetic Resonance	240
10 6	Preparation of Alcohols	243
10 7	Reactions of Alcohols	247
10 8	Nomenclature of Ethers	259
10 9	Physical Properties of Ethers	260
10 10	Preparation of Ethers	261
10 11	Reactions of Ethers	263
10 12	Cyclic Ethers	265
	PROBLEMS	270
<b>11.</b>	<b>Alkenes</b>	277
11 1	Electronic Structure	277
11 2	Nomenclature of Alkenes	281
11 3	Physical Properties of Alkenes	283
11 4	Relative Stabilities of Alkenes Heats of Formation	290
11 5	Preparation of Alkenes	293
11 6	Reactions of Alkenes	302
	PROBLEMS	327
<b>12.</b>	<b>Alkynes</b>	334
12 1	Electronic Structure	334
12 2	Nomenclature	335
12 3	Physical Properties	336
12 4	Acidity of Alkynes	339
12 5	Preparation of Alkynes	340
12 6	Reactions of Alkynes	346
12 7	Vinyl Halides	352
	PROBLEMS	353
<b>13.</b>	<b>Aldehydes and Ketones</b>	357
13 1	Structure	357
13 2	Nomenclature	358
13 3	Physical Properties	361
13 4	Nuclear Magnetic Resonance	363
13 5	Synthesis of Aldehydes and Ketones	366
13 6	Enolization	369
13 7	Carbonyl Addition Reactions	378
13 8	Oxidation and Reduction	399
	PROBLEMS	406
<b>14.</b>	<b>Infrared Spectroscopy</b>	412
14 1	The Electromagnetic Spectrum	412
14 2	Molecular Vibration	414
14 3	Characteristic Group Vibrations	418
14 4	Alkanes	420
14 5	Alkenes	420
14 6	Alkynes	421
14 7	Alkyl Halides	423
14 8	Alcohols and Ethers	423
14 9	Aldehydes and Ketones	424
14 10	Summary Principal Functional Group Absorptions	426

14 11 Instrumentation	428
PROBLEMS	429
<b>15. Organometallic Compounds</b>	437
15 1 Nomenclature	437
15 2 Structure	437
15.3 Physical Properties	440
15 4 Preparation of Organometallic Compounds	441
15 5 Reactions of Organometallic Compounds	447
15.6 Transition Metal Organometallic Compounds	454
PROBLEMS	460
<b>16. Organic Synthesis</b>	464
16 1 Introduction	464
16 2 Considerations in Synthesis Design	464
16 3 Planning a Synthesis	467
16 4 Protecting Groups	475
16 5 Industrial Synthesis	476
PROBLEMS	477
<b>17. Mass Spectrometry</b>	479
17 1 Introduction	479
17 2 Instrumentation	480
17 3 The Molecular Ion. Molecular Formula	482
17 4 Fragmentation	485
PROBLEMS	492
<b>18. Carboxylic Acids</b>	498
18 1 Structure	498
18 2 Nomenclature	499
18 3 Physical Properties	500
18.4 Acidity	501
18 5 Spectroscopy	507
18.6 Synthesis	509
18.7 Reactions	511
18.8 Occurrence of Carboxylic Acids	521
PROBLEMS	522
<b>19. Derivatives of Carboxylic Acids</b>	526
19.1 Structure	526
19 2 Nomenclature	528
19 3 Physical Properties	531
19 4 Spectroscopy	532
19 5 Basicity of the Carbonyl Oxygen	535
19 6 Hydrolysis: Nucleophilic Addition-Elimination	539
19 7 Other Nucleophilic Substitution Reactions	546
19 8 Reduction	554
19.9 Acidity of the $\alpha$ -Protons	558
19.10 Reactions of Amides That Occur on Nitrogen	563
19 11 Pyrolytic Eliminations	564
19.12 Waxes and Fats	566
PROBLEMS	570

<b>20. Conjugation</b>	575
20.1 Allylic Systems	575
20.2 Dienes	587
20.3 Unsaturated Carbonyl Compounds	595
20.4 Higher Conjugated Systems	612
20.5 The Diels-Alder Reaction	613
PROBLEMS	619
<b>21. Ultraviolet Spectroscopy</b>	624
21.1 Electronic Transitions	624
21.2 $\pi \rightarrow \pi^*$ Transitions	625
21.3 $n \rightarrow \pi^*$ Transitions	627
21.4 Alkyl Substituents	630
21.5 Other Functional Groups	632
21.6 Photochemical Reactions	633
PROBLEMS	634
<b>22. Benzene and the Aromatic Ring</b>	637
22.1 Benzene	637
22.2 Substituted Benzenes	646
22.3 Spectra	652
22.4 Dipole Moments in Benzene Derivatives	658
22.5 Side-Chain Reactions	661
22.6 Reduction	670
22.7 Aromaticity	675
PROBLEMS	685
<b>23. Electrophilic Aromatic Substitution</b>	690
23.1 Halogenation	690
23.2 Protonation	694
23.3 Nitration	695
23.4 Friedel-Crafts Reactions	697
23.5 Orientation in Electrophilic Aromatic Substitution	702
23.6 Theory of Orientation in Electrophilic Aromatic Substitution	706
23.7 Quantitative Reactivities Partial Rate Factors	712
23.8 Effects of Multiple Substituents	714
23.9 Synthetic Utility of Electrophilic Aromatic Substitution	717
PROBLEMS	721
<b>24. Amines</b>	725
24.1 Structure	725
24.2 Nomenclature of Amines	727
24.3 Physical Properties of Amines	729
24.4 Basicity	734
24.5 Quaternary Ammonium Compounds	740
24.6 Synthesis of Amines	742
24.7 Reactions of Amines	753
24.8 Enamines	767
PROBLEMS	770

<b>25. Other Nitrogen Functions</b>	780
25 1 Nitro Compounds	780
25 2 Isocyanates, Carbamates, and Ureas	785
25 3 Azides	786
25 4 Diazo Compounds	787
25 5 Diazonium Salts	790
PROBLEMS	803
<b>26. Sulfur and Phosphorus Compounds</b>	806
26 1 Thiols and Sulfides	806
26 2 Preparation of Thiols and Sulfides	808
26 3 Reactions of Thiols and Sulfides	809
26 4 Sulfate Esters	813
26 5 Sulfonic Acids	816
26 6 Phosphines and Phosphonium Salts	824
26 7 Phosphate and Phosphonate Esters	825
26 8 Sulfur- and Phosphorus-Stabilized Carbanions	830
PROBLEMS	834
<b>27. Difunctional Compounds</b>	839
27 1 Introduction	839
27 2 Nomenclature of Difunctional Compounds	840
27 3 Diols	844
27 4 Hydroxy Aldehydes and Ketones	851
27 5 Hydroxy Acids	856
27 6 Dicarboxylic Acids	861
27 7 Diketones, Keto Aldehydes, Keto Acids, and Keto Esters	871
PROBLEMS	866
<b>28. Carbohydrates</b>	892
28 1 Introduction	892
28 2 Stereochemistry and Configurational Notation of Sugars	894
28 3 Cyclic Hemiacetals Anomerism, Glycosides	897
28 4 Conformations of the Pyranoses	902
28 5 Reactions of Monosaccharides	903
28 6 Relative Stereochemistry of the Monosaccharides	
The Fischer Proof	918
28 7 Oligosaccharides	921
28 8 Polysaccharides	926
28 9 Sugar Phosphates	929
28 10 Natural Glycosides	931
PROBLEMS	932
<b>29. Amino Acids, Peptides, and Proteins</b>	935
29 1 Introduction	935
29 2 Structure, Nomenclature, and Physical Properties of	
Amino Acids	936
29 3 Acid-Base Properties of Amino Acids	939
29 4 Synthesis of Amino Acids	942
29 5 Reactions of Amino Acids	949
29 6 Peptides	951
29 7 Proteins	969
PROBLEMS	978

<b>30. Aromatic Halides, Phenols, Phenyl Ethers, and Quinones</b>	982
30.1 Introduction	982
30.2 Preparation of Halobenzenes	982
30.3 Reactions of Halobenzenes	985
30.4 Nomenclature of Phenols and Phenyl Ethers	992
30.5 Preparation and Properties of Phenols and Ethers	994
30.6 Reactions of Phenols and Ethers	1000
30.7 Quinones	1014
PROBLEMS	1023
<b>31. Polycyclic Aromatic Hydrocarbons</b>	1030
31.1 Nomenclature	1030
31.2 Biphenyl	1031
31.3 Naphthalene	1037
31.4 Anthracene and Phenanthrene	1048
31.5 Higher Polybenzenoid Hydrocarbons	1052
PROBLEMS	1055
<b>32. Heterocyclic Compounds</b>	1061
32.1 Introduction	1061
32.2 Nonaromatic Heterocycles	1062
32.3 Furan, Pyrrole, and Thiophene	1069
32.4 Condensed Furans, Pyrroles, and Thiophenes	1077
32.5 Azoles	1082
32.6 Pyridine	1089
32.7 Quinoline and Isoquinoline	1098
32.8 Diazines	1103
32.9 Pyrones and Pyrylium Salts	1106
PROBLEMS	1109
<b>33. The Chemical Literature</b>	1115
33.1 Research Journals	1115
33.2 Books and Review Articles	1116
33.3 Abstract Journals	1118
33.4 Beilstein	1121
PROBLEMS	1124
<b>34. Special Topics</b>	1126
34.1 The Hammett Equation: An Example of a Linear Free Energy Relationship	1126
34.2 Pericyclic Transition States	1133
34.3 Organic Coloring Matters	1147
34.4 Photochemistry	1155
34.5 Nucleic Acids	1161
34.6 Natural Products: Terpenes, Steroids, and Alkaloids	1165
34.7 Biosynthesis	1174
34.8 Stereoselective Synthesis	1183
<b>APPENDIX I Heats of Formation</b>	1191
<b>APPENDIX II Bond-Dissociation Energies</b>	1194
<b>APPENDIX III Average Bond Energies</b>	1195

<b>APPENDIX IV</b>	Acidity and Basicity	1196
<b>APPENDIX V</b>	Proton Chemical Shifts	1199
<b>APPENDIX VI</b>	Infrared Bands	1200
<b>APPENDIX VII</b>	Symbols and Abbreviations	1203
<b>INDEX</b>		1205

# 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 millennia.

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 which persist in similar 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.



The invention and development of the still by the alchemists had an interesting consequence in another area—medicine. Through the Middle Ages, medicine was practiced as a mystical blend of magic and folklore. It had long been noticed that certain animal and plant substances seemed to possess curative powers. With the advent of the still, it became possible to concentrate the “essence” of various natural materials. The use of various distillates as medical remedies quickly became a widespread practice. For several hundred years, physicians and their associates distilled all manner of natural substances. In the process, a number of relatively pure organic compounds were isolated, such as acetic acid from vinegar and formic acid from ants.

During this pre-1600 period, as the tools for handling matter were being developed and as numerous relatively pure chemical substances were being discovered, there was relatively little serious experimentation and no advance at all in the theory of matter. However, during the seventeenth and eighteenth centuries, chemistry was born as a science in Europe. The first area of serious investigation was gases. Although Boyle, Cavendish, Priestley, and Scheele made important breakthroughs, it was Lavoisier who laid the real foundation for modern chemistry. During this period, there evolved the notion of elements and combining weights. By 1789, Lavoisier had assembled a Table of the Elements, containing 33 substances, most of which appear in the modern periodic table.

In this formative stage in the science of chemistry, the substances derived from the animal and vegetable worlds were largely ignored. These materials were recognized as being different—more complex—than the compounds of the atmosphere or those compounds derived from the mineral kingdom. Lavoisier himself noted that **organic compounds**, as they came to be known, differed from the inorganic compounds in that they all seemed to be composed of carbon and hydrogen and occasionally nitrogen or phosphorus. For a time it was thought that organic compounds did not obey the new law of definite proportions, and people came to believe that a **vital force**, present only in living organisms, was responsible for the production of organic compounds.

The vitalism theory persisted until the middle of the nineteenth century. In 1828 Frederick Wöhler, working in Heidelberg, reported that, upon treating lead cyanate with ammonium hydroxide, he obtained urea. Since urea was a well-known organic compound, having been isolated from human urine by Roulle in about 1780, Wöhler had succeeded in preparing an organic compound in the laboratory for the first time. Although the synthesis of urea was recognized by the leading chemists of the day, the concept of vitalism did not die quickly. It was not until the synthetic work of Kolbe in the 1840s and Berthelot in the 1850s that the demise of vitalism was complete.

At this time, chemists recognized that it was not the vital force which imparted uniqueness to organic chemistry but rather the **simple fact that organic compounds are all compounds of carbon**. This definition—**organic chemistry is the chemistry of carbon compounds**—has persisted.

Simultaneously with the discovery of methods for the laboratory preparation of a multitude of organic compounds, analytical methods were also being perfected. With the advent of these methods, particularly the technique of combustion analysis, organic chemistry began to take on new dimensions. For the first time accurate formulas were available for fairly complicated organic compounds. There ensued a confusing period, which lasted from about 1800 until about 1850, during which various theories were advanced in an attempt to explain such complexities as isomerism (the existence of two compounds with the same formula) and substitution (the substitution of one element for another in a complex organic formula).