

*Organic  
Chemistry*

CRAM  
and  
HAMMOND

# *Organic Chemistry*

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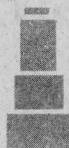
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## *Preface*

The remarkable growth of organic chemistry during the last twenty years has created serious problems for the teacher, particularly with respect to elementary courses. The introduction of new and valuable theoretical concepts into conventional schemes of presentation has been particularly difficult. In most textbooks, theory appears as an appendage to otherwise self-consistent and classical discussions organized around the important classes of organic compounds. As a result, modern texts have assumed an encyclopedic character. In an attempt to cope with this problem, the authors of this book have developed a novel approach to elementary organic chemistry.

In courses that we have taught in our respective universities, we have tried to find a new basis of organization which would both be economical and reflect recent advances in the field. By thorough integration of fact and theory, we tried to produce a fundamental course into whose pattern could be introduced, without disruption or unmanageable growth, the results of research as they became available. We found that facts were best taught when collated by theory, and that theory was most thoroughly understood when illustrated and developed through facts. By use of such a blend, we were able to minimize the taxonomic aspects of organic chemistry and to stress principles. This book is the product of our experimentation.

The first four chapters deal with structure, nomenclature, occurrence, and uses of the main classes of compounds. A few simple chemical reactions are introduced here to illustrate the interconversion of functional groups and to show the principles involved in degradative structure determination. Chapter 5 treats the chemical bond in terms of both resonance and molecular-orbital methods. In Chapter 6 stereochemistry is discussed in terms of bond angles and distances, free and restricted rotation about bonds; symmetry properties of molecules, and the configurations of ring compounds. Chapter 7 presents the relationships between physical prop-

erties and structure of organic compounds. Chapter 8 introduces the subject of correlation of structure with chemical reactivity. Acid-base reactions, familiar to students from their study of general chemistry, are used as a vehicle to illustrate resonance, inductive, and steric effects. Chapter 9 explains our scheme for classification of organic reactions and introduces reaction mechanisms. Chapters 8 and 9 provide a transition between the static and dynamic descriptions of organic chemistry.

In Chapters 10 through 20 reactions are discussed class by class. Although reactions fall naturally into three main categories—substitution, addition, and elimination—these classes have been subdivided to reduce discussions to convenient lengths. *The classification is operational rather than mechanistic*, although discussions of reaction mechanisms naturally fit easily into the scheme. Preparative methods are stressed, and synthetic sequences are frequently presented as units.

The last nine chapters are concerned with timely and useful special topics. Included are a chapter on heterocyclic compounds, three chapters on natural products (grouped according to biogenetic relationships), a chapter on natural and synthetic polymers, and chapters on petroleum, spectra, nomenclature, and chemical literature.

In a sense, we have attempted to examine organic chemistry from three different points of view. The first group of chapters treats relationships based on structure; the second group emphasizes the relationship among organic reactions; and the third group illustrates associations based upon the origin, use, and chemical technology of organic compounds. Thus students are given a thorough introduction to the descriptive part of the subject before they are exposed to a comprehensive treatment of reactions, and they have a good grasp of fundamental concepts of both structure and reactivity before they encounter the subject of complex molecules and their reactions. In this scheme, the important facts and concepts are repeatedly reviewed in varying contexts. The problems that appear at the end of each chapter serve to illustrate and develop the principles introduced in the text. In each set, there are at least two problems which are unusually difficult and which will stimulate the better students to think originally.

We believe that certain further advantages are associated with this organization. Chemical reactions and their applications to synthesis are introduced only after the structures of *both reactant and product* are familiar to the student. The early introduction of stereochemistry and theories of chemical reactivity allows these concepts to be used throughout the discussions of reactions. The organization of reactions into classes allows consideration of mechanism, scope, limitations, and side reactions to be applied to whole groups of transformations. Many subjects such as physical properties, acid-base theory, structure elucidation, spectra, nomenclature, and bibliography, which are ordinarily scattered, are given integrated treatment. The relationship between laboratory and lecture is strengthened by introduction in the first four chapters of enough struc-

tural concepts and reactions to provide a background for laboratory work for at least a term. The discussions of physical properties and acid-base reactions early in the course serve as useful adjuncts to laboratory work.

The book obviously includes more material than can be presented in a single course; however, in every chapter except the first four, sections of material may be omitted without loss of continuity. We have found that this flexibility allows the teacher to stress whichever of the three general sections he chooses. Thus a course designed for both chemistry and nonchemistry majors could emphasize the material in the first and third sections, whereas a course designed only for chemistry majors might stress the second group of chapters.

Our greatest ambition in writing this book has been to bring students in their first course closer to the frontiers of organic chemistry. We hope that our organization eliminates the waste usually involved in reorientation of students' thinking when they pass from an elementary course either to an advanced course or to research. If this book serves these purposes, we have succeeded.

We are indebted to many persons who contributed to this book. Professors Corwin Hansch and G. Ross Robertson served us well as critics during the preparation of the second draft of the manuscript. Our graduate students and postdoctoral fellows provided us with generous helpings of criticism of the manuscript, and they exercised tolerance and good judgment when our preoccupation with writing left them with an unusually large measure of independence in their research efforts. Others who read parts of the manuscript and offered helpful criticism include Professors Lawrence Bartell, Jerome Berson, Charles DePuy, Edward Leete, Harden McConnell, and Peter Yates, and Drs. John Hogg and Jay Kochi. Dr. John Schaefer read the entire page proof.

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# Contents

Preface v

CHAPTER 1	<b>INTRODUCTION</b>	1
	<i>Nature of Organic Chemistry, 1</i>	
	<i>History, 2</i>	
	<i>Characterization of Organic Compounds, 4</i>	
	<i>The Electron Pair as a Chemical Bond, 8</i>	
	<i>Structural Formulas of Organic Compounds, 10</i>	
	<i>Organic Reactions, 13</i>	
	<i>Organization of Book, 14</i>	
	<i>Problems, 14</i>	
CHAPTER 2	<b>HYDROCARBONS</b>	16
	<i>Classification, 16</i>	
	<i>Structure and Nomenclature, 17</i>	
	<i>Elucidation of Structure, 26</i>	
	<i>Occurrence and Uses, 30</i>	
	<i>Problems, 33</i>	
CHAPTER 3	<b>COMPOUNDS WITH FUNCTIONAL GROUPS SATURATED AT CARBON</b>	34
	<i>Structure, Nomenclature, and Properties, 34</i>	
	<i>Reactions, 48</i>	
	<i>Elucidation of Structure, 54</i>	
	<i>Problems, 56</i>	
CHAPTER 4	<b>COMPOUNDS WITH FUNCTIONAL GROUPS UNSATURATED AT CARBON</b>	58
	<i>Structure, Nomenclature, and Properties, 58</i>	
	<i>Reactions, 72</i>	
	<i>Synthesis, 81</i>	
	<i>Problems, 85</i>	

CHAPTER 5	<b>CHARACTER OF THE CHEMICAL BOND</b>	87
	<i>Atomic Structure, 87</i>	
	<i>Resonance, 92</i>	
	<i>Electrons as Waves, 98</i>	
	<i>Rules for Resonance Structures, 108</i>	
	<i>Resonance Energy, 109</i>	
	<i>Problems, 110</i>	
CHAPTER 6	<b>STEREOCHEMISTRY</b>	112
	<i>Bond Angles and Bond Lengths, 112</i>	
	<i>Rotation about Single Bonds, 113</i>	
	<i>Restricted Rotation about Double Bonds, 118</i>	
	<i>Geometric Isomerism, 119</i>	
	<i>Cyclic Compounds, 122</i>	
	<i>Molecular Asymmetry, 127</i>	
	<i>Carbon as an Asymmetric Center, 129</i>	
	<i>Many Asymmetric Centers per Molecule, 132</i>	
	<i>Racemization and Epimerization, 137</i>	
	<i>Stereoisomerism in Ring Compounds, 138</i>	
	<i>Resolution of Racemates into Enantiomers, 139</i>	
	<i>Asymmetric Centers Other than Carbon, 141</i>	
	<i>Absolute Configuration and Notation, 142</i>	
	<i>Systematic Specification of Configuration, 144</i>	
	<i>Problems, 145</i>	
CHAPTER 7	<b>PHYSICAL PROPERTIES</b>	147
	<i>Physical Properties as Means of Identification and Separation, 147</i>	
	<i>Intermolecular Interactions, 151</i>	
	<i>Correlations between Physical Properties and Structure, 158</i>	
	<i>Problems, 162</i>	
CHAPTER 8	<b>CORRELATION OF STRUCTURE AND REACTIVITY</b>	165
	<i>Proton Acids and Bases, 165</i>	
	<i>Effect of Medium, 167</i>	
	<i>Structural Effects, 168</i>	
	<i>Lewis Acids and Bases, 179</i>	
	<i>Tautomerism, 182</i>	
	<i>Problems, 184</i>	
CHAPTER 9	<b>CHARACTERIZATION OF ORGANIC REACTIONS</b>	187
	<i>Classes of Bond-making and Bond-breaking Processes, 187</i>	
	<i>Classes of Organic Reactions, 189</i>	
	<i>Organic Reaction Mechanisms, 191</i>	
	<i>Problems, 197</i>	



CHAPTER 10	<b>NUCLEOPHILIC SUBSTITUTION REACTIONS AT SATURATED CARBON</b>	199
	<i>Formation of Carbon-Oxygen Bonds, 201</i>	
	<i>Formation of Carbon-Sulfur Bonds, 212</i>	
	<i>Formation of Carbon-Nitrogen Bonds, 213</i>	
	<i>Formation of Carbon-Halogen Bonds, 216</i>	
	<i>Formation of Carbon-Hydrogen Bonds, 218</i>	
	<i>Carbon as a Nucleophile, 219</i>	
	<i>Organometallic Compounds, 220</i>	
	<i>Formation of Carbon-Carbon Bonds, 222</i>	
	<i>Scope of the Nucleophilic Substitution Reaction, 228</i>	
	<i>Problems, 229</i>	
CHAPTER 11	<b>MECHANISMS AND REACTIVITY IN THE NUCLEOPHILIC SUBSTITUTION REACTION</b>	231
	<i>Nucleophilic Substitution Mechanisms, 231</i>	
	<i>Kinetic Characteristics, 234</i>	
	<i>Steric Course of Substitution, 234</i>	
	<i>Carbonium-ion Rearrangements, 239</i>	
	<i>Further Reactivity Relationships, 240</i>	
	<i>Problems, 245</i>	
CHAPTER 12	<b>ELECTROPHILIC SUBSTITUTION AT SATURATED CARBON</b>	248
	<i>Formation of Carbon-Metal Bonds, 249</i>	
	<i>Formation of Carbon-Halogen Bonds, 253</i>	
	<i>Formation of Carbon-Oxygen and Carbon-Sulfur Bonds, 256</i>	
	<i>Formation of Carbon Bonds to Other Hetero Atoms, 257</i>	
	<i>Formation of Carbon-Hydrogen Bonds, 257</i>	
	<i>Formation of Carbon-Carbon Bonds, 263</i>	
	<i>Stereochemistry of Electrophilic Substitution Reactions, 264</i>	
	<i>Problems, 266</i>	
CHAPTER 13	<b>NUCLEOPHILIC ADDITION TO UNSATURATED CARBON</b>	268
	<i>Carbon-Halogen Bond Formation, 269</i>	
	<i>Carbon-Oxygen and Carbon-Sulfur Bond Formation, 271</i>	
	<i>Carbon-Nitrogen Bond Formation, 277</i>	
	<i>Carbon-Hydrogen Bond Formation, 278</i>	
	<i>Carbon-Carbon Bond Formation, 282</i>	
	<i>Organometallic Reagents in Carbonyl Additions, 294</i>	
	<i>Nucleophilic Addition to Carbon-Carbon Double Bonds, 296</i>	
	<i>Synthesis of Alcohols, 297</i>	
	<i>Problems, 299</i>	

CHAPTER 14	<b>NUCLEOPHILIC SUBSTITUTION AT UNSATURATED CARBON</b>	301
	<i>Carbon-Halogen Bond Formation, 301</i>	
	<i>Carbon-Oxygen Bond Formation, 303</i>	
	<i>Carbon-Sulfur Bond Formation, 313</i>	
	<i>Carbon-Nitrogen Bond Formation, 313</i>	
	<i>Carbon-Hydrogen Bond Formation, 319</i>	
	<i>Carbon-Carbon Bond Formation, 321</i>	
	<i>Cyclization Reactions, 327</i>	
	<i>Acid-catalyzed Acylation, 331</i>	
	<i>Problems, 332</i>	
CHAPTER 15	<b>ELECTROPHILIC AND OTHER ADDITION REACTIONS</b>	334
	<i>Carbon-Halogen Bond Formation, 334</i>	
	<i>Carbon-Oxygen Bond Formation, 339</i>	
	<i>Carbon-Nitrogen Bond Formation, 344</i>	
	<i>Carbon-Hydrogen Bond Formation, 345</i>	
	<i>Carbon-Carbon Bond Formation, 346</i>	
	<i>Free-radical Addition, 347</i>	
	<i>Cyclic Additions, 350</i>	
	<i>Catalytic Hydrogenation, 352</i>	
	<i>Problems, 355</i>	
CHAPTER 16	<b>ELECTROPHILIC SUBSTITUTION AT UNSATURATED CARBON</b>	357
	<i>Substituent Effects, 358</i>	
	<i>Carbon-Halogen Bond Formation, 363</i>	
	<i>Carbon-Oxygen Bond Formation, 365</i>	
	<i>Carbon-Sulfur Bond Formation, 365</i>	
	<i>Carbon-Nitrogen Bond Formation, 368</i>	
	<i>Carbon-Hydrogen Bond Formation, 371</i>	
	<i>Carbon-Carbon Bond Formation, 372</i>	
	<i>Carbenes as Electrophiles, 387</i>	
	<i>Problems, 389</i>	
CHAPTER 17	<b>ELIMINATION REACTIONS</b>	394
	<i>Carbon-Carbon Double-bond Formation, 395</i>	
	<i>Olefin Synthesis, 407</i>	
	<i>Carbon-Carbon Triple-bond Formation, 408</i>	
	<i>Carbon-Oxygen Bond Formation, 410</i>	
	<i>Carbon-Nitrogen Triple-bond Formation, 411</i>	
	<i>Problems, 411</i>	

CHAPTER 18	<b>HOMOLYTIC SUBSTITUTION REACTIONS</b>	414
	<i>Stable Free Radicals</i> , 414	
	<i>Generation of Transient Radicals</i> , 416	
	<i>Carbon-Halogen Bond Formation</i> , 418	
	<i>Carbon-Oxygen Bond Formation</i> , 419	
	<i>Carbon-Nitrogen Bond Formation</i> , 420	
	<i>Carbon-Hydrogen Bond Formation</i> , 421	
	<i>Carbon-Carbon Bond Formation</i> , 422	
	<i>Photochemical Addition and Reduction</i> , 423	
	<i>Problems</i> , 424	
CHAPTER 19	<b>OXIDATION AND REDUCTION</b>	426
	<i>Oxidation</i> , 427	
	<i>Reduction</i> , 441	
	<i>Problems</i> , 450	
CHAPTER 20	<b>MOLECULAR REARRANGEMENTS</b>	452
	<i>Rearrangement of Electron-deficient Systems</i> , 453	
	<i>Rearrangement of Electron-rich Systems</i> , 466	
	<i>Migration of Double and Triple Bonds</i> , 469	
	<i>Rearrangement to an Aromatic Nucleus</i> , 474	
	<i>Problems</i> , 477	
CHAPTER 21	<b>HETEROCYCLIC COMPOUNDS</b>	479
	<i>Five-membered Rings</i> , 479	
	<i>Fused Systems with Five-membered Rings</i> , 484	
	<i>Six-membered Rings</i> , 486	
	<i>Fused Six-membered Ring Systems</i> , 491	
	<i>Problems</i> , 495	
CHAPTER 22	<b>CARBOHYDRATES AND PHENOLIC PLANT PRODUCTS</b>	497
	<i>Monosaccharides</i> , 498	
	<i>Disaccharides</i> , 511	
	<i>Glycosides</i> , 513	
	<i>Natural Products Related to Saccharides</i> , 514	
	<i>Phenolic Plant Products</i> , 517	
	<i>Problems</i> , 523	
CHAPTER 23	<b>AMINO ACIDS, PEPTIDES, AND ALKALOIDS</b>	526
	<i>Amino Acids</i> , 527	
	<i>Peptides</i> , 530	
	<i>Alkaloids</i> , 533	
	<i>Problems</i> , 548	



CHAPTER 24	<b>LIPIDS, TERPENES, AND STEROIDS</b>	550
	<i>Lipids</i> , 550	
	<i>Waxes</i> , 554	
	<i>Fatty Acids from Microorganisms</i> , 554	
	<i>Isoprenoids</i> , 555	
	<i>Steroids</i> , 560	
	<i>Problems</i> , 569	
CHAPTER 25	<b>NATURAL AND SYNTHETIC POLYMERS</b>	570
	<i>Vinyl Polymers</i> , 571	
	<i>Condensation Polymers</i> , 578	
	<i>Natural Polymers</i> , 580	
	<i>Polysaccharides</i> , 580	
	<i>Proteins</i> , 585	
	<i>Physical Properties of Polymers</i> , 590	
	<i>Problems</i> , 594	
CHAPTER 26	<b>PETROLEUM CHEMISTRY</b>	597
	<i>Composition of Petroleum</i> , 598	
	<i>The Reactions of Petroleum Technology</i> , 601	
	<i>Isomerization</i> , 602	
	<i>Cracking</i> , 603	
	<i>Alkylation and Polymerization</i> , 608	
	<i>Hydrogenation in Petroleum Refining</i> , 609	
	<i>Hydrocarbon Oxidation</i> , 610	
	<i>Other Sources of Motor Fuels</i> , 611	
	<i>Problems</i> , 612	
CHAPTER 27	<b>SPECTRA AND DYES</b>	613
	<i>Absorption Spectra</i> , 613	
	<i>Visible and Ultraviolet Spectra</i> , 617	
	<i>Infrared Spectra</i> , 624	
	<i>Raman Spectra</i> , 626	
	<i>Nuclear Magnetic Resonance Absorption</i> , 627	
	<i>Dyes</i> , 629	
	<i>Dyeing</i> , 630	
	<i>Chemical Classes of Dyes</i> , 630	
	<i>Problems</i> , 643	
CHAPTER 28	<b>NOMENCLATURE</b>	645
	<i>Common Names</i> , 645	
	<i>Derived Names</i> , 653	
	<i>IUC System</i> , 657	
	<i>Other Systematic Nomenclature</i> , 662	
	<i>Miscellaneous Nomenclature</i> , 662	
	<i>Problems</i> , 665	

## CHAPTER 29 LITERATURE OF ORGANIC CHEMISTRY

668

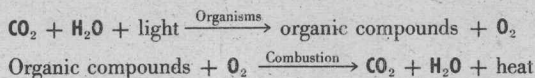
*Advanced Textbooks*, 669*Reference Books*, 670*Reviews of Research Literature*, 672*Handbooks and Dictionaries of Organic Compounds*, 673*Encyclopedias of Organic Compounds*, 673*Abstracts*, 675*Basic Literature*, 676*Literature Search for a Particular Organic Compound*, 677*Problems*, 677*Index* 679





Organic compounds constitute most of the materials associated with living organisms. This fact accounts for the name given the field, for it was thought once that only living organisms could synthesize organic compounds. Although the great bulk of naturally occurring organic materials have been photosynthesized by plants and microorganisms from carbon dioxide, water, and nitrogen, many compounds can now be prepared in the laboratory from carbon, hydrogen, water, nitrogen, and oxygen.

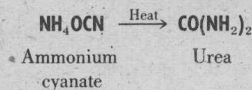
The chief sources of organic materials are coal, petroleum, natural gas, wood, and agricultural products. The property common to all these substances and to almost all organic substances is that they are fuels and burn to produce carbon dioxide and water with the liberation of heat. Our deposits of coal and petroleum are huge energy reservoirs. This point can be illustrated through two highly simplified equations.



## History

Although people have been deliberately carrying out organic reactions since the discovery of fire, the field was not elevated from an art to a science until the nineteenth century. The ensuing development can be roughly divided into three overlapping periods.

The beginning of the first period is lost in the advance of chemistry as a general science, an advance that gathered momentum toward the latter part of the eighteenth century. This was a period of groping, of trial and error, a period when the prejudices of medieval beliefs affected much of the thought concerning natural processes. "Organic compounds" were supposed to contain a characteristic "vital force" out of which life processes were made. This *vitalistic theory* was later dismissed by numerous experiments demonstrating that "organic compounds" could be prepared from inorganic materials. One of the first experiments of this type was carried out by Wöhler (in 1828), who converted ammonium cyanate, an inorganic compound, to urea, which had been known as an organic compound because of its presence in human urine.



The main advances of this period were of a general chemical nature, and lay in the recognition of the power of elemental analysis and molecular weight determination, which provided data leading to molecular formulas.

The second period started in 1859 with the birth of the *structural theory* of organic compounds. Seldom in history had an idea borne more fruit than the simple concept advanced by Kekulé and Couper

that organic molecules possess structural features, with *atoms of carbon* as the main building blocks and *chemical bonds* as the mortar. The ability of carbon to form strong bonds to carbon, hydrogen, oxygen, nitrogen, sulfur, and halogens provides the foundations for the science. The structural theory supplied a basis for determining the order in which different atoms are bonded to one another in a molecule. The resulting *sequence formulas* gave a rational explanation for the existence of the great variety of organic compounds that were known even at that time. A third dimension was added to organic formulas by the hypothesis advanced by van't Hoff and Le Bel in 1874 that the four bonds of carbon are directed toward the corners of a tetrahedron, at the center of which the carbon atom is situated. This hypothesis for the first time brought molecular architecture into organic chemistry, and provided an explanation for many observations that the structural theory in its early form failed either to explain or to represent.

Elaboration of the rules governing the structure and formation of organic compounds occupied the efforts of organic chemists through the end of the nineteenth century, until World War I. This exciting "classical period" was marked by two major endeavors: the construction of compounds through organic reactions; the elucidation of the structures of organic substances by molecular degradation. During this time, *ball-and-stick models* allowed the chemist to visualize structures of organic compounds, the balls representing atoms, and the sticks representing bonds.

The third, or "modern," period, which began with the end of World War I, has been one of refinement and exploitation. During this phase organic chemistry has derived considerable inspiration from the related fields of physical chemistry and physics. Extensive correlations of physical and chemical properties with molecular structure have been elaborated. Such correlations allow chemists to specify a set of properties desired in a product, to predict what molecular structures will have these properties, and to synthesize by rational means compounds possessing these structures.

The world has been in an "Organic Chemical Age" for almost thirty years, and the era is just reaching maturity. Multimillion-dollar industries based on organic compounds have taken their places alongside the other commercial giants of our civilization. Farm products, wood, coal, petroleum, and natural gas have been chemically tailored to provide organic products that vitally affect our environment. Fabrics, dyes, paints, coatings, and structural materials literally surround us. Rubber takes the violence out of movement, gasoline fuels our travel, gas both warms and cools our houses, plastics fashion our implements, and drugs guard our health and prolong our lives. Unprecedented opportunities to exercise the imagination are available in organic research, and much still remains to be done. The cultural movement of the twentieth century is in the hands of the scientists, and the organic chemist is playing a prominent role in providing direction for this movement.

### **Characterization of Organic Compounds**

One of the goals of organic chemistry is to achieve complete descriptions of individual organic compounds. General procedures have evolved which can be applied to most organic compounds and which provide a step-by-step approach to the final goal, the detailed structural formula. This section of the book is devoted to a description of those steps which permit a compound to be thoroughly enough characterized so that it may be distinguished from all other compounds.

**Molecular Homogeneity.** Every organic compound possesses a distinct set of physical and chemical properties that differentiates it from every other compound. The physical properties most commonly used for characterizing a compound are melting point, boiling point, adsorption behavior, and interactions (absorption, refraction, diffraction, and rotation) with light and other radiation. Common techniques for separating organic compounds from one another are differential extraction, crystallization, distillation, and adsorption. A compound is usually considered pure if its physical (and sometimes chemical) properties do not change when it is subjected to procedures based on the above techniques.

**Qualitative Elemental Analysis.** Once pure, a compound is further characterized by identification of its elements. If the compound burns in air, one knows that carbon and hydrogen are probably present, particularly if the flame contains soot. In another procedure, molecular destruction of the substance by fusion with sodium metal converts any nitrogen, sulfur, or halogen into inorganic salts, which can be detected by appropriate qualitative tests.

**Quantitative Elemental Analysis and Molecular Formulas.** In quantitative combustion analysis, a weighed portion of a compound is burned in oxygen over hot copper oxide at about 700°. Carbon dioxide and water are produced in essentially 100% yields, and are individually captured and weighed in absorption tubes. This is accomplished by first passing the combustion gases through a tube containing magnesium perchlorate (Anhydrone), which absorbs the water vapor and converts it to water of hydration; then by leading them through a tube containing finely divided sodium hydroxide (Ascarite), which absorbs and converts the carbon dioxide to sodium carbonate.

The *per cent composition* of carbon and hydrogen in the unknown compound can be calculated by utilizing the stoichiometric principles of general chemistry. Should the sum of these percentages equal approximately 100%, no other elements are present in the molecule. If the sum is less than 100%, and qualitative tests reveal the absence of elements such as nitrogen, sulfur, and halogens, then oxygen is probably present. Frequently the oxygen content is assumed to be the difference between the sum of the percentages of carbon and hydrogen and 100%. A better procedure involves the direct determination of oxygen content by decom-