A Handbook of Organic Chemistry

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Dr. Narendrasinh B Gohil

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Preface

Organic chemistry is the scientific study of the structures, properties, and methods of syntheses of chemical compounds that are based on carbon. This field stands in a complementary relationship to inorganic chemistry, which covers the study of the compounds of all other elements, as well as the elements themselves. These two disciplines are generally considered separately, but there is much overlap, such as in the sub-discipline of organometallic chemistry. Organic compounds are primarily composed of carbon and hydrogen, and may contain any number of other elements, the most common of which are nitrogen and oxygen. Each carbon atom, with its pattern of forming four covalent bonds, can connect with other carbon atoms in a variety of ways to give the enormous diversity of organic compounds found. Each molecule is often described as having a "skeleton" of carbon atoms. The essential indication for existence and relationship inherent in four-based structures is appropriate for carbon, as it is one of the bases of life itself. Important classes of organic compounds include the alkanes, alkenes, alkynes, aromatic compounds, alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, amines, and amides. Many organic compounds—such as carbohydrates, amino acids, proteins, lipids, nucleotides, and nucleic acids—are found in living systems. The study of organic chemistry has led to enormous benefits in practical terms, such as in the production of textiles, paints, plastics, fuels, and pharmaceuticals. The field of organic chemistry includes more than twenty million compounds for which properties have been determined and recorded in the literature. Many hundreds of new compounds are added every day. Much more than half of the world's chemists are organic chemists. Some new organic compounds are simply isolated from plants or animals; some are made by modifying naturally occurring chemicals; but most new organic compounds are actually synthesized in the laboratory from other (usually smaller) organic molecules. Over the years organic chemists have developed a broad array of reactions that allow them to make all kinds of complex products from simpler starting materials.

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Introduction

Organic chemistry is the branch of chemistry that focuses on the properties and reactions of compounds that contain carbon atoms. The carbon atom is unique because it is the only element that can bond to it, forming chains that can contain hundreds of atoms. Carbon can also combine with a wide variety of other elements. Compounds are based on the chemistry of carbon. Carbon is unique in the variety and extent of structures that can result from the three-dimensional connections of its atoms. The process of photosynthesis converts dioxide and water to oxygen and compounds known as carbohydrates. Both cellulose, the substance that gives structural rigidity to plants, and starch, the energy storage product of plants, are polymeric carbohydrates. Simple carbohydrates produced by photosynthesis form the raw material for the myriad organic compounds found in the plant and animal kingdoms. When combined with variable amounts of hydrogen, oxygen, nitrogen, sulfur, phosphorus, and other elements, the structural possibilities of carbon compounds become limitless, and their number far exceeds the total of all nonorganic compounds. A major focus of organic chemistry is the isolation, purification, and structural study of these naturally occurring substances. Many natural products are simple molecules. Examples include formic acid (HCO_2H) in ants, ethyl alcohol(C_2H_5OH) in fermenting fruit, and oxalic acid ($C_2H_2O_4$) in rhubarb leaves. Other natural products, such as penicillin, vitamin B_{12}, proteins, and nucleic acids, are exceedingly complex. The isolation of pure natural products from their host organism is made difficult by the low concentrations in which they may be present. Once they are isolated in pure form, however, modern instrumental techniques can reveal structural details for amounts weighing as little as one-millionth of a gram. The correlation of the physical and chemical properties of compounds with their structural features is the domain of physical organic chemistry.

Once the properties endowed upon a substance by specific structural units termed functional groups are known, it becomes possible to design novel molecules that may exhibit desired properties. The preparation, under controlled

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laboratory conditions, of specific compounds is known as synthetic chemistry. Some products are easier to synthesize than to collect and purify from their natural sources. Tons of vitamin C, for example, are synthesized annually.

Many synthetic substances have novel properties that make them especially useful. Plastics are a prime example, as are many drugs and agricultural chemicals. A continuing challenge for synthetic chemists is the structural complexity of most organic substances. To synthesize a desired substance, the atoms must be pieced together in the correct order and with the proper three-dimensional relationships. Just as a given pile of lumber and bricks can be assembled in many ways to build houses of several different designs, so too can a fixed number of atoms be connected together in various ways to give different molecules. Only one structural arrangement out of the many possibilities will be identical with a naturally occurring molecule. The antibiotic erythromycin, for example, contains 37 carbon, 67 hydrogen, and 13 oxygen atoms, along with one nitrogen atom. Even when joined together in the proper order, these 118 atoms can give rise to 262,144 different structures, only one of which has the characteristics of natural erythromycin. The great abundance of organic compounds, their fundamental role in the chemistry of life, and their structural diversity have made their study especially challenging and exciting. Organic chemistry is the largest area of specialization among the various fields of chemistry.

HISTORY

Prehistoric civilizations obtained many useful chemicals from plants and animals. They were familiar with sugar, which they learned to ferment to make wine. Then they found that the wine could turn into vinegar. Ancient Egyptians used blue dye made from the indigo in madder root, and a royal purple dye extracted from a rare kind of mollusk. Soap was made by heating animal fat with base from wood ashes.

During the Middle Ages dry distillation of wood yielded mixtures of methyl alcohol, acetone, and acetic acid. Alchemists isolated cholesterol from gallstones, morphine from opium, and drugs such as quinine, strychnine, and brucine from various plants. Two hundred years ago chemists such as Antoine Lavoisier determined the elemental composition of many of these substances and noted that they all contained carbon and hydrogen, and that many also contained oxygen and nitrogen. It also appeared that there were two classes of materials: the mineral type (generally hard, high-melting, and noncombustible), and the organic type (often soft, liquid or low melting solids, and frequently easily combustible materials). Most organic chemicals could be burned to produce carbon dioxide; and any hydrogen present was converted to water (H_2O). Because organic compounds had for centuries been isolated only from plants and animals, it was commonly believed that some "vital force" in living things was necessary to produce them. This belief persisted until 1828, when Friedrich

Wöhler was able to make urea, a chemical found in the urine of animals, from the inorganic salt ammonium cyanate.

Since that time organic chemistry has grown into a vast and ever expanding field that encompasses millions of chemical compounds.

More than a million carbon compounds have been discovered, and new ones are constantly being synthesized. One reason for this large number is isomerism, particularly structural isomerism, first recognized in 1830 by the Swedish chemist Jöns Jakob Berzelius (1779–1848). In this arrangement, two or more compounds contain the same number of carbon and hydrogen atoms arranged in different ways to form unique compounds with distinct chemical and physical properties. A compound formed from five carbons and twelve hydrogen atoms ($C_5 H_{12}$) will, for example, produce three unique compounds. Other forms of isomerism distinguished by the spatial arrangements of their atoms were discovered later in the nineteenth century.

In the eighteenth and early part of the nineteenth centuries, when many carbon-based compounds were first isolated, they had only been extracted from plants and animals. For example, formic acid had been isolated from ants, salicylic acid had been isolated from willow bark, and urea had been found in urine. This entrenched the idea that organic molecules must be created by (or by the actions of) a living organism. This idea also fit with the doctrine known as vitalism, a theory that developed in reaction to the rise of the mechanistic approach to life being merely a physical process.

The Influence of Liebig and Wöhler

Two German chemists, Justus von Liebig (1803–1873) and Friedrich Wöhler (1800–1882), were responsible for the emergence of organic chemistry in the early nineteenth century. Their quantitative analytical methods helped establish the constitution of newly isolated and synthesized carbon compounds. Both were inspiring teachers who established laboratory work as the basic model for chemical education, teaching students who came from all over Europe and America. The pupils then emulated their methods when they returned home to train the next generation of chemists.

Liebig, the most prominent chemist in nineteenth-century Europe, studied chemistry at the Universities of Bonn and Erlangen, where he obtained his PhD in 1822. After further study in Paris, he chaired the chemistry department at the University of Giessen before moving to the University of Munich, where he spent the remainder of his life. Liebig's major contributions were the development of new methods for the quick and precise measurement of the quantities of carbon, hydrogen, and nitrogen in organic compounds. This allowed Liebig and his students to identify a host of new organic compounds. Much of his work after 1840 was related to agricultural and biological chemistry, including a study of fermentation and methods for increasing soil fertility and yields through the use of artificial fertilizers.

The Synthesis of Urea and the Demise of Vitalism

Wöhler studied medicine at the Universities of Marburg and Heidelberg, obtaining his medical degree in 1823. He went on to study with Berzelius in Stockholm and to hold positions in technical schools in Berlin and Kassel. In 1836 he was appointed professor of chemistry in the medical faculty of Göttingen University, a position he held for the rest of his life. Wöhler's major research interests were in inorganic chemistry, where he isolated the elements boron, silicon, aluminum, cerium, and just missed being the discoverer of vanadium and niobium. Like Liebig, he also established a school of research and teaching, but is best known for synthesizing urea.

In 1828 Wöhler synthesized the organic compound urea in the laboratory using the inorganic compound ammonium cyanate. Urea had previously been found only in urine—that is, from a biological source. While this dealt a blow to vitalism, it did not fully spell its demise. Skeptics believed that compounds associated with living organisms were produced by a "vital force" not available to the chemist. This idea persisted until 1844 when Hermann Kolbe (1818–1884) proved definitively that organic compounds could be produced under laboratory conditions by synthesizing acetic acid from the simple inorganic compounds carbon disulfide and chlorine.

Structural Theory and Its Development

In the early part of the nineteenth century a new problem emerged as chemists tried to classify and bring some order to the ever-increasing number of organic substances. This began a period of confusion and controversy that would last several decades, until the development of the structural theory of organic chemistry.

Analytical methods pioneered by both Liebig and Wöhler were able to determine the content of organic molecules, but did not show how their elements were arranged. The first attempt to solve the problem was known as radical theory. Berzelius proposed a way to understand the formation of inorganic compounds by assuming that some elements had a positive charge and others had a negative charge. Scientists knew that opposite electrical charges would attract; thus the formation of sodium chloride could be explained by assuming that sodium is positively charged and chlorine is negatively charged.

Radical theory was pioneered in the 1830s by Liebig and the French chemist Jean-Baptiste André Dumas (1800–1884). Radicals were thought to be a stable group of elements that were joined together to produce an electropositive group that was joined to an electronegative atom to form a compound. In the case of organic compounds the radical would contain carbon, hydrogen, and various other atoms in combination with an electronegative inorganic partner. Thus ethyl alcohol was represented as $C_2H_4 H_2O$.

The electropositive radical was capable of transformation but should remain intact. This was demonstrated by Liebig and Wöhler in the case of benzaldehyde,

which was extracted from almonds. The fact that compounds made from benzaldehyde all contained the radical $C_{14}H_{10}O_2$provided evidence for radical theory.

Radical theory lost its hold on organic chemistry, however, when scientists realized it was possible to substitute one atom for another in what was assumed to be a "stable" radical. This substitution was further shown by Dumas to be an atom of a different charge. For example, in some compounds the substitution of electronegative chlorine for electropositive hydrogen did not significantly change the character of the product. Dumas were able to convert acetic acid to trichloroacetic acid, and the product still remained an acid.

Radical theory gave way in the 1840s to what became known as type theory. It was developed by two of Dumas's students, Auguste Laurent (1808–1853) and French chemist Charles Frédéric Gerhardt (1816–1856), who proposed that organic (and even inorganic) substances were derived from simple molecules by substitution. Alexander Williamson (1824–1904) experimentally proved the existence of the water type with his synthesis in 1850 of diethyl ether from the potassium salt of ethyl alcohol and ethyl iodide.

In 1845 Laurent also introduced the concept of 2 homologous series—a group of similar compounds that differed by a single unit. The first three members of the alkane series, for example, are methane (CH_4), ethane (CH_6), and propane (C_3H_8); each succeeding molecule contains an additional CH_2 group. The German chemist Hermann Kopp (1817–1892) showed that each additional CH_2 increases the boiling point of each successive group member by a fixed number of degrees.

Three other types were proposed by Gerhardt in 1853, the ammonia (NH_3), hydrogen (H_2), and hydrogen chloride (HCl) types. These types together with the water type could be used to classify the already large number of organic compounds into four distinct groupings. Gerhardt wrote "By exchanging their hydrogen's among certain groups, these types give rise to acids, to alcohols, to ethers, to hydrides, to radicals, to organic chlorides, to acetones, to alkalis." Type theory was thus an advance—but because it still allowed multiple classifications for the same molecule, major problems remained to preoccupy chemists in the latter part of the nineteenth century.

Valences The concept of valence (the combining power of an element) slowly developed in the period from 1850 to 1870 through the work of the English chemist Edward Frankland (1825–1899) and the German August Kekulé (1829–1896). Frankland had begun his chemical studies in London and continued them in Germany with chemist Robert Wilhelm Bunsen (1811–1899) at Marburg. Frankland's view of valence was derived from the earlier radical theory; Kekulé's was based on type theory.

Frankland attempted to synthesize the hydrocarbon radical ethyl (C_2H_5) by reacting ethyl iodide with zinc. This produced not the desired result but butane, with diethyl zinc, the first example of an organometallic compound, as a byproduct. What was crucial about this discovery was that the diethyl zinc

$(C_2H_5)2Zn$ always contained twice as much ethyl as zinc. Frankland went on to show that in other organometallic compounds that a definite combining power existed between the organic portion and the metal. In 1852 Frankland proposed that inorganic and organic compounds both had 5 a combining power that came to be known as valence. Frankland also recognized multiple valences and gave examples where the valence was 3 or 5 such as in PCl3 & PCl_5.

August Kekulé

Friedrich August Kekulé (1829–1896) was born in Darmstadt Germany, a descendent of a noble Bohemian family from Stradonitz, a city near Prague. Kekulé had studied architecture at Geissen, but because of Liebig's influence he changed to chemistry, with additional studies in biological classification. Kekulé obtained his doctorate in Paris in 1851.

As a student in Paris, Kekulé had studied with Dumas and Gerhardt and was naturally drawn to type theory. Further study in London from 1854 to 1855 brought him into contact with two very original thinkers: Williamson and William Odling (1829–1921), chemists who studied chemical structure to understand chemical properties. Kekulé hypothesized that carbon was tetravalent, that is, could combine with four

Substituents to form organic molecules. His approach was purely mechanical and may have been influenced by his initial interest in architecture. In 1858 Kekulé proposed that carbon could form chains by using some of its valences to bond to other carbon atoms. Kekulé's representations are not the familiar structural formulas we use today. Those were established by Scottish chemist Archibald Scott Couper (1831–1892) in 1858.

Couper had studied in Paris with the French chemist Charles-Adolphe Wurtz (1817–1884). He had ideas similar to those of Kekulé, but due to a series of mishaps his paper was published after Kekulé's, and thus he failed to receive the credit he should have. In contrast to the conservative and cautious Kekulé, Couper drew formulas for molecules that used dotted lines to represent the bonds between carbon atoms.

The graphical structural formulas that are used today were introduced by Alexander Crum Brown (1838–1922) in 1861. Initially he wrote the elements using the letters such as C, H, O, etc., with circles around them, as Dalton had done in his exposition of the atomic theory in the first decade of the nineteenth century. The circles were connected with solid lines, with the number of lines equal to the valence—four in the case of carbon. The circles were eventually dropped to create the structural formulas we still use today.

Stereochemistry and Aromaticity

The idea that molecules are three dimensional was not realized until the latter part of the nineteenth century. Discoveries made by French scientist Louis Pasteur (1822–1895), Dutch chemist Jacobus van't Hoff (1852–1911), and French

chemist Joseph-Achille Le Bel (1847–1930) provided the keys to understanding the three-dimensional nature of many organic molecules.

Pasteur is best known for his microbiological research, but his initial training was in chemistry. In his doctoral research Pasteur studied the puzzling differences between two forms of the same compound: tartaric acid. Pasteur found that natural tartaric acid, isolated from the fermentation of grapes, rotated the polarization plane of light that passed through it. Racemic acid, a synthesized product that had an identical chemical formula, however, did not.

The French physicist Jean-Baptiste Biot (1774–1862) had observed this same phenomenon in 1815 with several organic liquids, including oil of turpentine. Salts of tartaric acid had been studied by other chemists as well, in particular the German chemist Eilhard Mitscherlich (1794–1863), who reported in 1844 that the physical properties of the sodium-ammonium salts of the optically active tartaric acid and the racemic acid were the same in every respect except their interaction with plane-polarized light.

Pasteur found that a comprehensive study of different tartrates showed that the optically active tartrates had an asymmetrical crystalline shape. All the racemic acid crystals were symmetrical. One particular compound, the sodium ammonium double salt of tartaric acid, produced very large well-defined crystals. Using a microscope and tweezers Pasteur was able to isolate two forms of the crystals. When subjected to plane polarized light, one bent the light to the right and the other to the left. The rotation was identical for both except the direction. If mixed in equal amounts there was no rotation at all. This phenomenon came to be known as stereoisomerism. Pasteur proposed that it was possible in nature for molecules to be asymmetric; by extension an association was made by Pasteur between asymmetry and life.

Pasteur and Kekulé had speculated that stereoisomerism might be caused by either the tetravalency of carbon itself or the way carbon is oriented in space as a result. This question was answered in 1874 by van't Hoff and Le Bel, independently of each other.

At this time van't Hoff was a professor in the veterinary school in Utrecht, Holland. His initial proposal, written in Dutch, attracted little attention. An extended form, La chimie dans l'espace(Chemistry in space) published in French in 1875, attracted much interest and controversy. He explained stereoisomerism by proposing that the four carbon valences were on the apexes of a tetrahedron. Four different substituents bonded to the central carbon atom could produce two structures that were mirror images of each other; this would then produce the asymmetry in carbon compounds.

Thus two mirror images could exist that were identical in all their properties except for the way they affected polarized light. These mirror images came to be known as enantiomers. Pasteur found that if a mixture contains equal amounts of each type, they cancel each other; this is why racemic acid did not affect polarized light and the natural tartaric acid did. Any mixture with equal numbers of enantiomers is now known as a racemic mixture.

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Le Bel's explanation was similar, but he started with a carbon that had four identical groups and looked at what happened with successively substituted atoms. With four different substituents, an asymmetry is produced in which the mirror image is no longer super-imposable on the original. Molecules that have more than one center of asymmetry (that is, more than one stereogenic center) will have 2 stereoisomers, where n is the number of sterogenic centers. In organic chemistry, each carbon atom to which four other atoms (or groups of atoms) are bonded constitutes a stereogenic center. Not every carbon atom in an organic molecule is necessarily a stereogenic center.

An example of how this rule applies is the glucose molecule (C 6H12 O 6), whose stereoisomers were first studied by German chemist Emil Fischer (1852–1919). Each glucose molecule has three centers of asymmetry, which allows the atoms to combine into $2^n = 8$ (eight) unique compounds, which Fischer identified. One of the major achievements of twentieth-century synthetic organic chemistry has been to develop methods to produce particular stereoisomers when multiple routes are possible.

One major structural problem that remained to be solved was the structure of benzene (C 6 H6) and aromatic compounds in general. Benzene was a formidable challenge because its unusual properties could not be based on conventional ideas of structure. Many chemists had tried and failed to solve the benzene problem before Kekulé devised the first rational structure in 1865.

In a story of dubious authenticity, Kekulé is said to have had a daydream in which he envisioned a snake catching its tail; this led him to visualize benzene's hexagonal structure, in which six carbon atoms alternate in single and double bonds. This model predicted that four unique isomers existed in disubstituted benzene molecules (benzene molecules containing two substituted atoms or groups of atoms), but only three were known. Kekulé proposed that one of these isomers has two forms that differ only by the locations of the single and double bonds. If an equilibrium exists between these two forms, all the carbon atoms become equivalent. This explanation became the basis of aromatic chemistry until the development of molecular orbital theory in the 1930s.

The Birth of the Synthetic Organic Chemical Industry

Organic compounds such as ethyl alcohol, found in beer and wine, and acetic acid, used in vinegar, have been produced since antiquity. Other naturally occurring organic compounds have been used for millennia as dyes and medicinal agents. But the production of organic substances in manufacturing plants did not being in earnest until the 1850s. The synthetic organic chemical industry began when a process was developed in the late-eighteenth century to produce gas from coal. This produced coal tar, a waste product that was considered a nuisance as it had only limited use, mainly as a water-proofing agent.

Organic chemists began to examine the constituents of coal tar in earnest in the 1840s. One of the primary investigators was the German chemist August