

CHAPTER 1

INTRODUCTION TO ORGANIC CHEMISTRY

1.1 Historical Background of Organic Chemistry

Organic chemistry is the area of chemistry that involves the study of carbon and its compounds. Carbon is now known to form a seemingly unlimited number of compounds. The uses of organic compounds impact our lives daily in medicine, agriculture, and general life.

In theory (Oparin, 1923) organic chemistry may have its beginnings with the big bang when the components of ammonia, nitrogen, carbon dioxide and methane combined to form amino acids, an experiment that has been verified in the laboratory (Miller, 1950). Organic chemicals were used in ancient times by Romans and Egyptians as dyes, medicines and poisons from natural sources, but the chemical composition of the substances was unknown.

In the 16th century organic compounds were isolated from nature in the pure state (Scheele, 1769) and analytical methods were developed for determination of elemental composition (Lavoisier, 1784).

Scientists believed (Berzelius, 1807) that organic chemicals found in nature contained a special "vital force" that directed their natural synthesis, and therefore, it would be impossible to accomplish a laboratory synthesis of the chemicals. Fortunately, later in the century Frederick Wöhler (1828) discovered that urea, a natural component in urine, could be synthesized in the laboratory by heating ammonium cyanate. His discovery meant that the natural "vital force" was not required to synthesis organic compounds, and paved the way for many chemists to synthesize organic compounds.

By the middle of the nineteenth century many advances had been made into the discovery, analysis and synthesis of many new organic compounds. Understanding about the structures of organic chemistry began with a theory of bonding called valence theory (Kekule, Couper, 1858).

Organic chemistry developed into a productive and exciting science in the nineteenth century. Many new synthetic methods, reaction mechanisms, analytical techniques and structural theories have been developed. Toward the end of the century much of the knowledge of organic chemistry has been expanded to the

2 Ch 1 Introduction

study of biological systems such as proteins and DNA. Volumes of information are published monthly in journals, books and electronic media about organic and biological chemistry.

The vast information available today means that for new students of organic chemistry a great deal of study is required. Students must learn about organic reactions, mechanism, synthesis, analysis, and biological function.

The study of organic chemistry, although complex, is very interesting, and begins here with an introduction of the theory of chemical bonding.

1.2 The Chemical Bond

1.2a Atomic Theory

The atomic theory of electrons began in the early 1900s and gained acceptance around 1926 after Heisenberg and Schroedinger found mathematical solutions to the electronic energy levels found in atoms, the field is now called quantum mechanics.

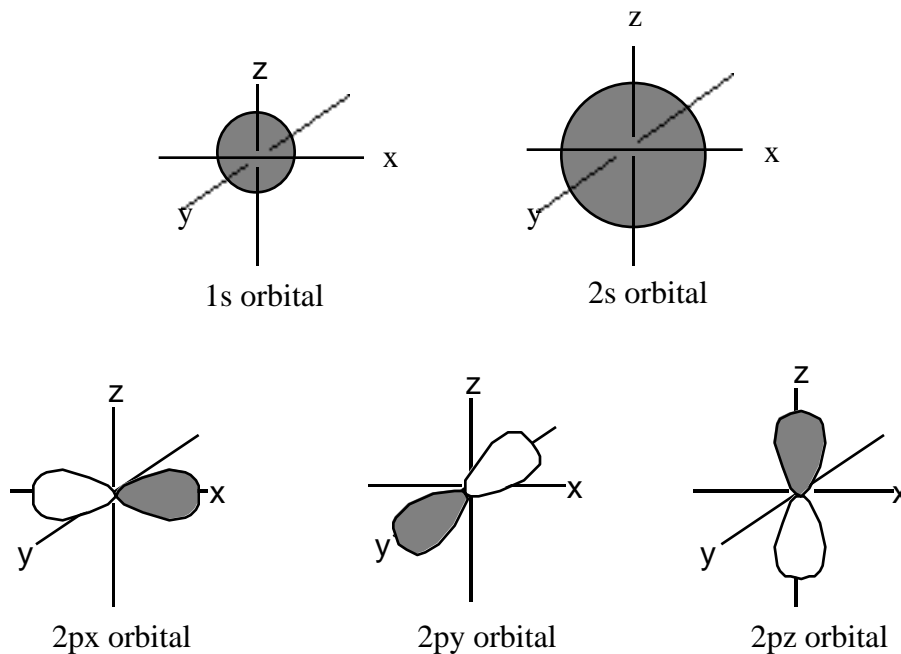
Electrons exist in energy levels that surround the nucleus of the atom. The energy of these levels increases as they get farther from the nucleus. The energy levels are called shells, and within these shells are other energy levels, called subshells or orbitals., that contain up to two electrons. The calculations from atomic theory give the following results for electron energy and orbitals. The results for the first two energy levels (shells 1 and 2) are the most important for bonding in organic chemistry.

Shell	Orbitals				Total Electrons Possible
	s	p	d	f	
1	1				2
2	2	3			8
3	3	3	5		18
4	1	3	5	7	32

***energy level 1** contains up to two electrons in a spherical orbital called a 1s orbital.

***energy level 2** contains up to eight electrons; two in an 2s-orbital and two in each of three orbitals designated as 2p-orbitals. The p-orbitals have

a barbell type shape and are aligned along the x, y, and z axes. They are thus called the px, py, and pz orbitals.



***energy level 3** contains up to eighteen electrons, two electrons in a 3s orbital, six electrons in the three 3p orbitals, and ten electrons in the five 3d orbitals.

***energy level 4** contains up to thirty-two electrons, two electrons in a 4s-orbital, six electrons in the three 4p-orbitals, ten electrons in the five 4d-orbitals, and fourteen electrons in the seven 4f-orbitals.

Electrons fill the lower energy levels first until all of the electrons are used (Aufbau Principle). An element contains the number of electrons equal to its atomic number. For the first and second row elements the electron configurations are relatively simple.

Element (atomic number)	Electron Configuration
H (1)	$1s^1$ (1st shell, s orbital, one electron)
He (2)	$1s^2$
Li (3)	$1s^2, 2s^1$

4 Ch 1 Introduction

Be (4)	$1s^2, 2s^2$
B (5)	$1s^2, 2s^2, 2p^1$
C (6)	$1s^2, 2s^2, 2p^2$
N (7)	$1s^2, 2s^2, 2p^3$
O (8)	$1s^2, 2s^2, 2p^4$
F (9)	$1s^2, 2s^2, 2p^5$
Ne (10)	$1s^2, 2s^2, 2p^6$ (inert, completely filled)

1.2b Electronegativity

Electronegativity is the ability of an atom to attract electrons to itself, and generally increases as one moves from left to the right across the periodic table.

least most
electronegative $\text{Li} < \text{Be} < \text{B} < \text{C} < \text{N} < \text{O} < \text{F}$ electronegative

Electronegativity also increases as we go from the bottom to the top of a column in the periodic table.

least most
electronegative $\text{I} < \text{Br} < \text{Cl} < \text{F}$ electronegative

Elements that easily lose electrons and attain a positive charge are called **electropositive** elements. Alkali metals are electropositive elements.

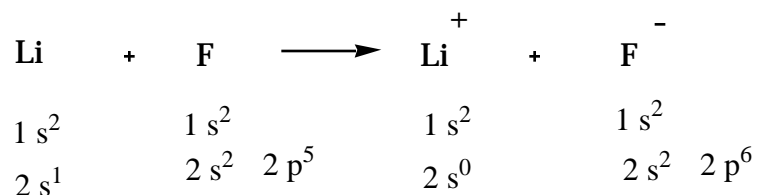
1.2c Bonding

Atoms can become bonded with each other, and their electronic structure governs the type of bond formed. The main two types of bonds that are formed are called **ionic** and **covalent**.

Ionic Bond

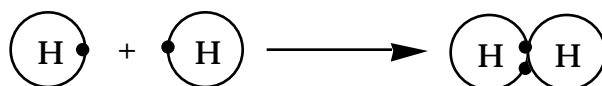
Ionic bonding is important between atoms of vastly different electronegativity. The bond results from one atom giving up an electron while another atom accepts the electron. Both atoms attain a stable noble gas configuration.

In the compound lithium fluoride, the $2s^1$ electron of lithium is transferred to the $2p^5$ orbital of fluorine. The lithium atom gives up an electron to form the positively charged lithium cation with $1s^2, 2s^0$ configuration, and the fluorine atom receives an electron to form a fluoride anion with $1s^2, 2s^2, 2p^6$ configuration. Thus the outer energy levels of both ions are completely filled. The ions are held together by the electrostatic attraction of the positive and negative ions.

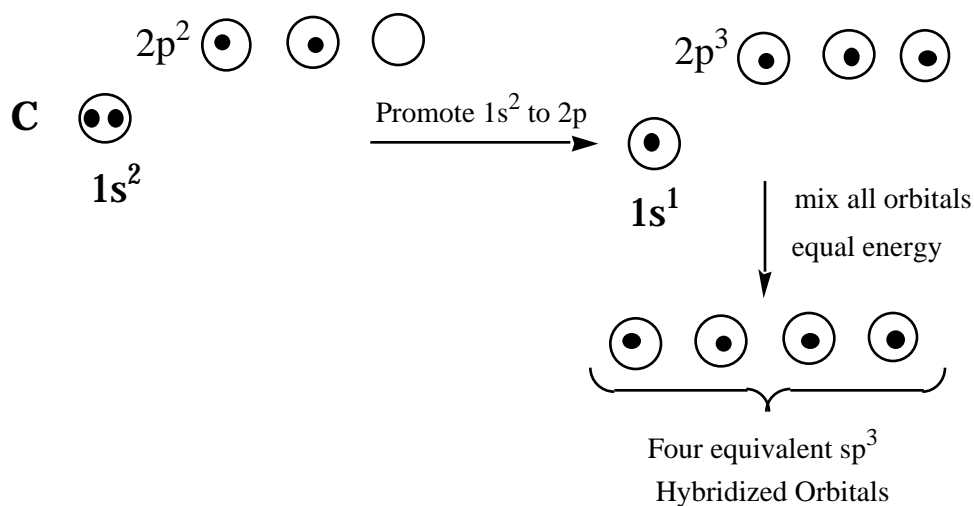
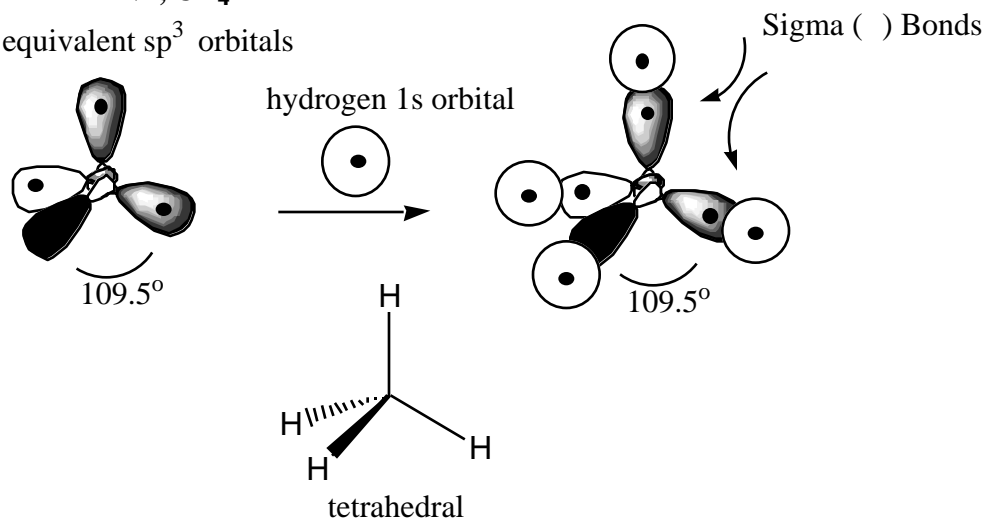


Covalent Bond

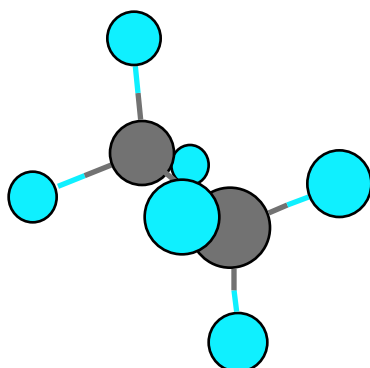
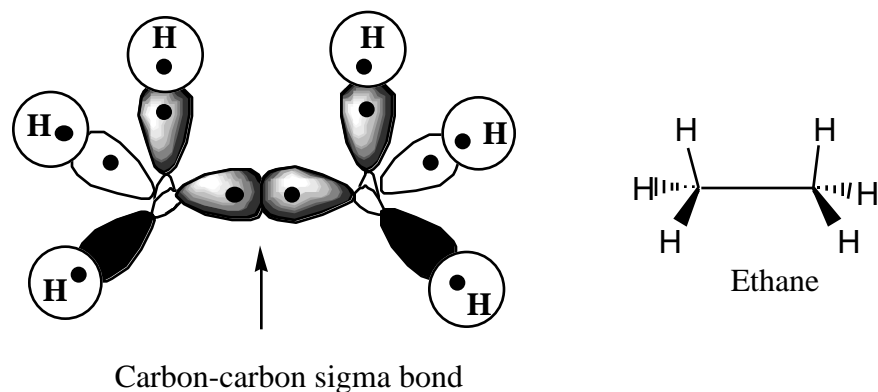
A **covalent bond** is formed by a sharing of two electrons by two atoms. A hydrogen atom possessing the $1s^1$ electron joins with another hydrogen atom with its $1s^1$ configuration. The two atoms form a covalent bond with two electrons by sharing their electrons.



In hydrogen fluoride, HF, the hydrogen $1s$ electron is shared with a $2p^5$ electron in fluorine ($1s^2, 2s^2, 2p^5$), and the molecule is now held together by a covalent bond. In this case, the fluorine atom is much more electronegative than the hydrogen atom and the electrons in the bond tend to stay closer to the fluorine atom. This is called a **polar covalent bond**, and the atoms possess a small partial charge denoted by the Greek symbol

CARBON-- sp^3 HYBRIDIZED**METHANE, CH_4** equivalent sp^3 orbitals

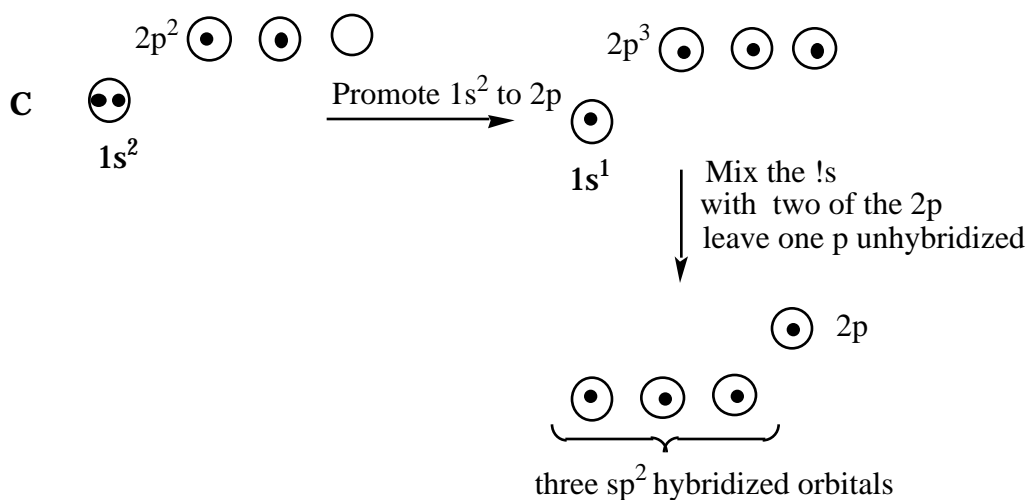
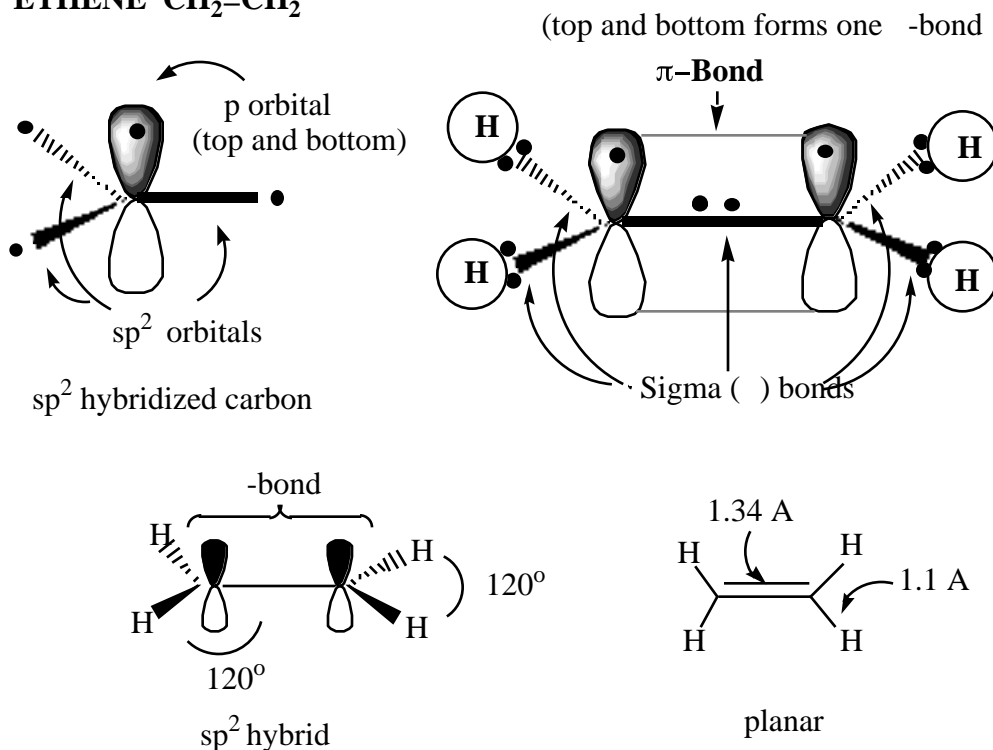
The unique property of carbon that differentiates it from the other elements and allows the formation of so many different organic compounds is the ability of carbon to bond with itself through covalent bonding. Thus, addition of another carbon atom to methane results in ethane which has covalent sigma bonds to the hydrogen atoms and a covalent sigma bond between the carbon atoms. Addition of more carbon atoms leads to many more compounds.



1.3b The Carbon-Carbon Double Bond-The Pi (π) Bond

Carbon forms a wide variety of compounds that contain carbon bonded to another carbon with a double bond between the two atoms. These compounds are classified as alkenes (older naming calls them olefins). The orbital model below explains the carbon-carbon double bond. The carbon electron configuration shows one s electron being promoted to a p orbital. But now only three orbitals are mixed, a s orbital and two p orbitals, that are called sp^2 hybrid orbitals and are used to form single bonds (sigma bonds). The p orbital contains one electron.

The combination of two of the sp^2 hybridized carbon atoms leads to two carbon atoms being joined by overlap of sp^2 orbitals to form a C-C single bond, and the side-to-side overlap of the p orbitals to form another bond known as a **pi** (π) bond. In the molecule of ethene shown below there are a total of 5 sigma bonds and one pi bond. As a result of the bonding in an ethene, the molecule is planar with bond angles of 120° and a C=C bond length that is longer than the C-H bond length.

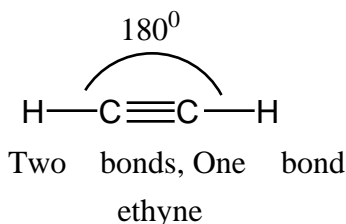
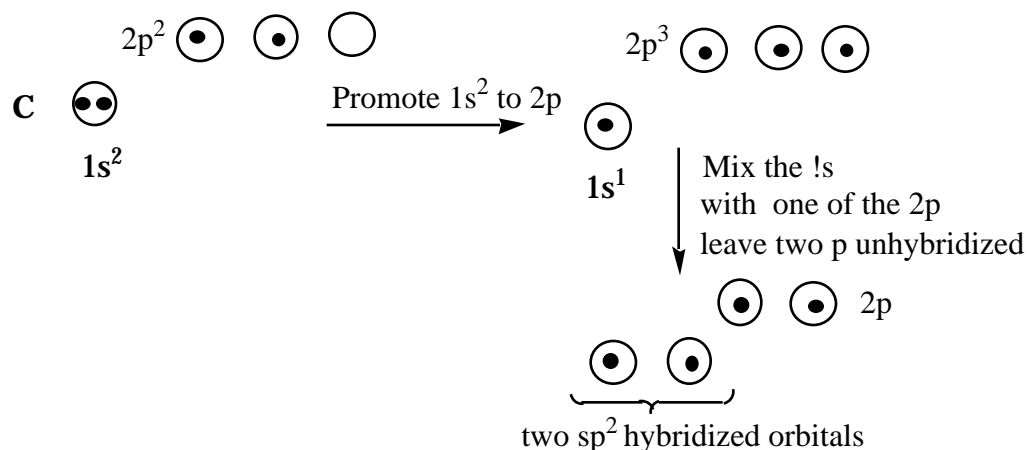
CARBON-- sp^2 HYBRIDIZED**ETHENE $CH_2=CH_2$** 

When carbon forms a bond with an electronegative atom such as oxygen, nitrogen, sulfur or a halogen, the bond is a polar covalent bond with the electrons of the bond residing closer to the electronegative atom.

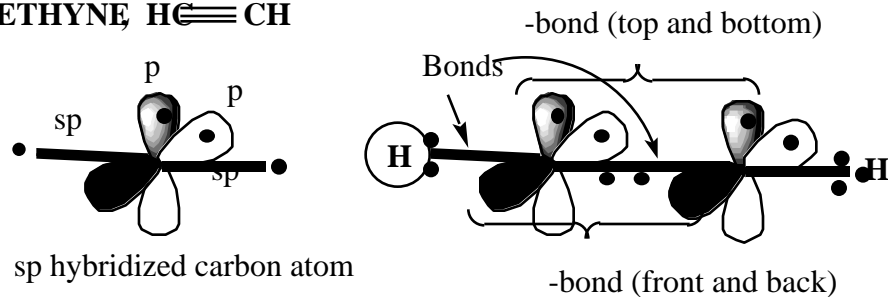
1.3c The Carbon-Carbon Triple Bond

Another type of bond that carbon forms with itself is the triple bond found in a class of compounds called alkynes. After promotion of the 2s electron to a 2p orbital, one s orbital mixes with one p orbital to give two hybrid sp orbitals. The two remaining p orbitals are used to make pi bonds. Thus the carbon is bound by a sigma bond to hydrogen from one of the sp hybrid orbital, to the other carbon atom by a sigma bond from one of the sp hybrid orbitals, and the two carbon atoms are bound by two pi bonds from side-to-side overlap of the two p orbitals. The sp hybrid orbitals position themselves 180° apart and thus a molecule of ethyne is linear with the hydrogen atoms 180° apart.

CARBON--sp HYBRIDIZED



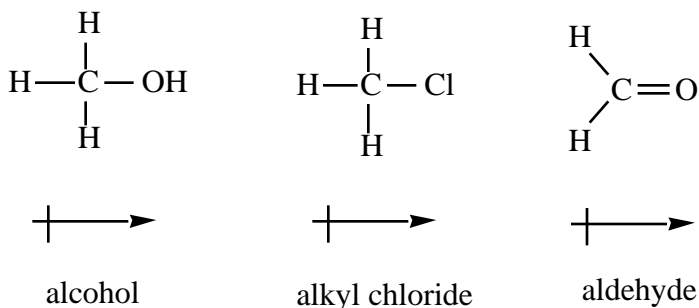
ETHYNE, $\text{HC} \equiv \text{CH}$



sp hybridized carbon atom

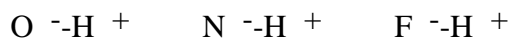
1.3d Polar Covalent Bonds in Carbon

Carbon forms single, double and triple bonds with elements other than carbon. The atoms involved in the bonding are usually oxygen, nitrogen, sulfur and the halogens. These elements are more electronegative than carbon and thus attract the electrons to themselves. The bonds are therefore **polar covalent bonds**. Bonds that contain a separation of charge possess a **dipole moment**, a property that contributes to the overall polarity of the molecule.



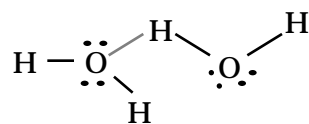
1.3e Hydrogen Bonds and Bond Polarity

The bonds O-H, N-H and F-H are highly polar covalent bonds because the electronegative draws electrons away from the hydrogen atom. In every case the hydrogen atom has a partial positive charge.

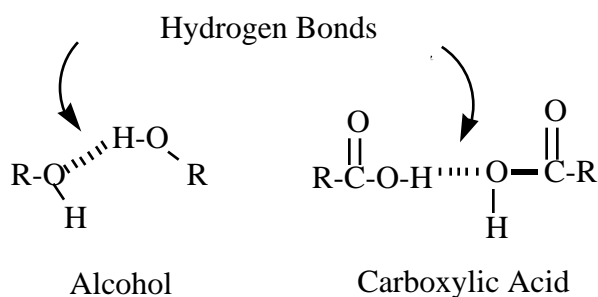


A result of molecules having these highly polarized bonds with the hydrogen atom partly positive in nature, the hydrogen atom is attracted to the basic site in other molecules, such as the non-bonding electrons on oxygen and nitrogen (non-bonding electrons are electrons belong to an element that complete the octet but do not participate in bonding). This attraction is called hydrogen bonding and is useful for explaining high boiling points and high melting points of fairly low mass molecules. Thus hydrogen bonding in water explains why the compound with only three atoms boils relatively high when compared with other molecules of similar mass. Extra energy is required to break the hydrogen bonds during the boiling process.

Hydrogen bonding in Water



In organic compounds hydrogen bonding is very important for describing the boiling and solubility characteristics of alcohols and acids, and the concept will be given in more detail in chapters dealing with those types of molecules.



(R stands for organic function)

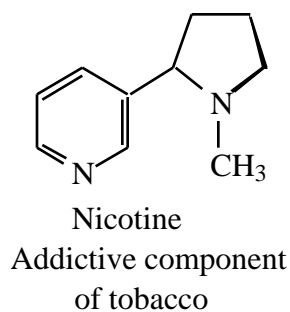
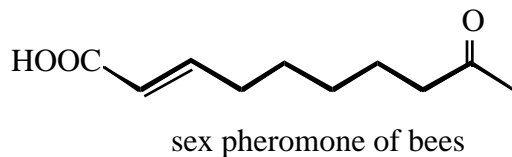
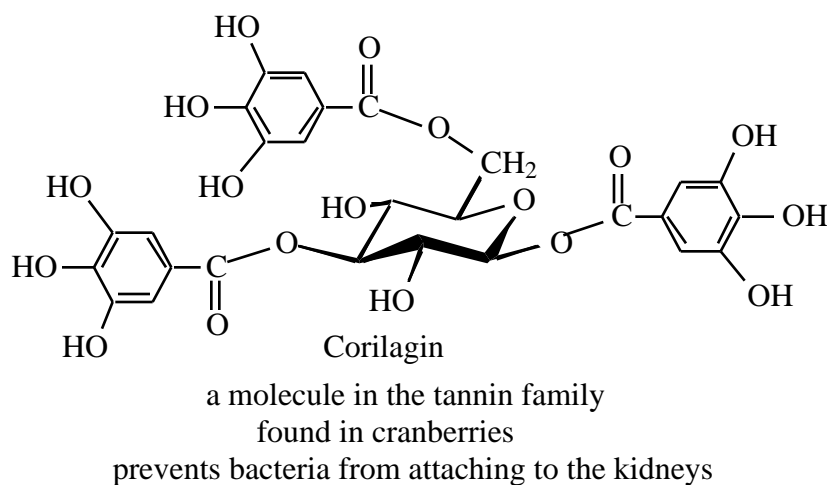
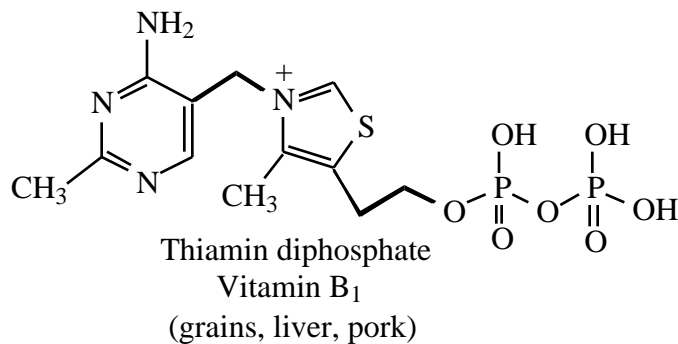
1.4 Organic Structures

At first the study of organic chemistry involves understanding the energy and shapes of simple organic structures. Then the study progresses to more complicated three-dimensional structures and finally to the investigation of reactions of organic molecules. We use the theories of bonding and the facts about acidic or basic properties of the molecules to understand the overall picture of what is happening. But the overall goal is to improve mankind through the development of new and better processes to be applied in medicine, agriculture and biomedical science, that is to make life better. Thus we must be able to study difficult molecules too.

As you proceed through organic chemistry you will write many different structures, and the writing gets easier with practice. But in the beginning it can be confusing. Always remember that carbon has four bonds!

In writing an alkane such as pentane which has five carbon atoms. We could write it by just showing carbon atoms, but it does not show carbon with four


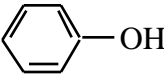
The structures of organic chemicals can be very complicated and very interesting. Sometime they are so complex that condensed structures are the only reasonable presentation. But as always, the carbon atom has four bonds. Several advanced organic structures are shown below.



1.5 Classification of Organic Compounds

Organic compounds are often classified according to the type (s) of functional groups present. These functional groups are presented in detail in the

remaining chapters. The on-sight recognition of functional groups is required for an adequate study of organic chemistry.

Alkane	CH_3CH_3	Alkene	$\text{CH}_2=\text{CH}_2$
Alkyne	$\text{HC}\equiv\text{CH}$	Alkyl Halide	R-halogen
Aromatic		Alcohol	R-OH
Phenol		Ether	R-O-R
Aldehyde	$\text{RCH}=\text{O}$	Ketone	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$
Acid	RCOOH	Ester	RCOOR
Anhydride	$(\text{RCO})_2\text{O}$	Amide	RCONH_2
Nitrile	RCN	Amine	R-NH_2

1.6 Summary

The science of Organic Chemistry has a broad and diverse past with many investigators from many countries making discoveries that when combined over 200 years led to the field of Organic Chemistry. The intrigue found with substances that contain carbon, organic compounds, arose because so many different substances could be found in nature and many of them had medicinal uses. The discovery of a laboratory synthesis of urea by *Frederich Wöhler* (1828) showed that organic chemicals did not have to be prepared by the vital forces of nature but could also be prepared by humans, thus opening the way for the field of synthetic organic chemistry.

The theory of bonding in chemicals achieved prominence because of the contributions by *Heisenberg and Schroedinger*, and many others. The electronic configuration of elements is seen as combination of electrons in specific energy levels called *shells* that further contain energy levels known as *subshells* with *s, p, d and f orbitals*. The ability of the elements to donate or share their electrons with other elements to form bonds is the basis for the formation of all compounds. When the elements form bonds by complete donation or acceptance of electrons the bonds form are called *ionic bonds*. Bonds in compounds that are formed from the sharing of two electrons are

called *covalent bonds*, and constitute the majority of bonds found in organic compounds. Carbon compounds contain the carbon atom in several hybridized states. The theory of hybridization, meaning that the electronic configuration of carbon is altered when it forms bonds, is required to explain the shapes and properties of organic compounds. Thus carbon is said to be hybridized in sp^3 , sp^2 , and sp *electronic configurations* that give rise to carbon single bonds called *sigma (σ) bonds*. The unhybridized p orbital in the sp^2 and sp configurations is used to form bonds called *pi (π) bonds*, that give rise to the double and triple bonds found in ethenes and ethynes respectively. The bonds from carbon to polar atoms are often polar and are called *polar covalent bonds*. Carbon compounds that contain OH and NH bonds give rise to *hydrogen bonding*, much like that found in water, and lead to a number of interesting chemical and physical properties.

The writing of chemical structures is extremely important in the study and practice of organic chemistry. **Of utmost importance is that when one writes or draws a structure another person can understand the structure.** Thus neatness is required. Many computer programs are available to assist with the writing of chemical structures. Organic structures can be written to show the complete structure with all the elements and bonds, but often this is too cumbersome. Thus various types of condensed structures can be written with the ultimate condensed structures written only with lines and an understanding of where the carbon and hydrogen atoms are located.

Carbon combines with many elements and itself to form a very wide variety of substances. *These substances are classified according to the exact type of substituent and bonding on the carbon atom.* The study of organic chemistry is often conducted by studying the individual classes of compounds as will be seen in the following chapters.

1.7 Problem Set

1.1 A famous scientist of the 20th century was Linus Pauling who received two Nobel prizes during his life. Look up a biography of Pauling and list his most notable contributions to science.

1.2 Sections 1.2a shows the electronic configuration for the 2nd row elements. Show the electronic configuration for the third row elements. Common ions in the 3rd row are Na^{+1} , Mg^{+2} , Al^{+3} , Si^{+4} , P^{+5} , S^{-2} , Cl^{-1} . What characteristic of their electronic configurations do these ions share that accounts for their stability?

1.3 The dipole moment (μ) of a molecule is the vector sum of the dipole moments of the individual bonds. In some cases these sums cancel each other while in other cases they enhance each other. Given the bond moments of H-C (0.4) and C-Cl (1.5), predict the dipole moment, and thus the polarity, of CH_3Cl , CH_2Cl_2 , CHCl_3 and CCl_4 .

1.4 For the compounds below write the complete structure and designate the bonding in each bond.

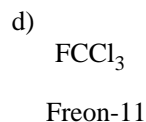
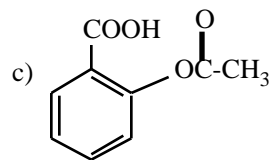
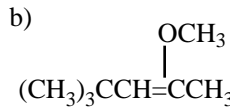
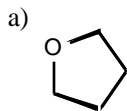
a) ethane, CH_3CH_3 b) propene, $\text{CH}_3\text{CH}=\text{CH}_2$ c) propyne

1.5 Hydrogen bonds in alcohols and carboxylic acids have a bond strength of 8-10 kcal/mole. The energy required to break these bonds explains the higher bp of hydrogen bonded substances. a) Use a chemical handbook to find the boiling points of the following compounds to see the effect of hydrogen bonding on the boiling point.

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ versus $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ versus $\text{CH}_3\text{CH}_2\text{COOH}$

b) What are the molecular weights for these compounds and how does the molecular weight affect the bp in them?

1.6 Expand the structures below to show all atoms and unshared electron pairs.



aspirin

1.7 Use the internet to locate several interesting sites for organic chemistry.