8. ORGANIC COMPOUNDS

Organic chemistry is the chemistry of the compounds of carbon. The name "organic" is a relic of the days when chemical compounds were divided into two classes, inorganic and organic, depending on their origin. Inorganics came from minerals; organics came from material produced by living matter. Originally, it was thought that organic compounds could only come from living matter, but today many organics are synthesized. Two major reservoirs of organic matter for synthesis are petroleum and coal. The focus of these notes is to provide a basis for understanding contaminant distribution and movement in the natural environment.

There are a plethora of synthetic organic compounds currently being produced and discarded. These are highly varied in properties and reactivities. The approach used in this course, based on the approach used in Schwarzenbach et al.(1993), is that understanding the chemical structure of organic molecules will provide a basis for predicting their behavior.

8.1 The Fundamentals

Elemental Composition-Molecular and structural formula

First we need to look at the atoms comprising organic compounds and the chemical bonds linking them. Organic molecules consist of a relatively small set of atoms: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), phosphorus (P) and halogens [iodine (I), chlorine (Cl), bromine (Br) and fluorine (F)]. Carbon can form stable C-C bonds, basically forming a carbon skeleton for organic molecules. Other atoms can substitute into this structure, allowing an almost infinite amount of stable organic structures to be synthesized.

To specify organic molecules, we need elemental composition and the molecular formula. That is not sufficient, however, because we also need to describe the spatial (or steric) structure. A given molecular formula could have a variety of spatial arrangements (these are referred to as *isomers.*) To understand this, we need to review the number and nature of bonds each element can form. To do this, we will compare the above atoms to the electronic structure of noble gases [helium (He), argon (Ar), krypton (Kr), xenon(Xe) and radon (Rn)]. Noble gases are especially non-reactive; these atoms contain filled shells. Argon was named after the Greek word "argos" or lazy; it was noted that argon was extremely non-reactive (see Table 1).

Bonding

Much of the chemistry of organic compounds can be described on the basis of atoms attaining the "filled shell" status, either by losing or gaining electrons, or more importantly by sharing electrons. The electrons in the outer shell are known as the valence electrons and they determine the chemistry of the atom. Refering to Table 1, we can see that C has four unfilled outer shells (hence the ability to form 4 bonds), N has 3 unfilled shells, O two unfilled shells and the halogens 1 unfilled shells Table 8.1. Atoms

with a valence of 2 or higher have multiple valences and are characterized by definite bond angles (e.g. in ammonia are 106^o46', water 104^o27').

Atomic Table 8.1. Mass, Electronic Configuration, and Typical Number of Covalent Bonds of the Most Important Elements Present in Organic Molecules*

Name	Element[a] Symbol	Number	Mass[b] (amu)	K	L	M	N	O	Net Charge of Kernel	Number Covalent Bonds Commonly Occurring in Organic Molecules
Hydrogen	H	1	1.008	1					1+	1
Helium	He	2		2					0	
Carbon	C	6	12.011	2	4				4+	4
Nitrogen	N	7	14.007	2	5				5+	3,(4)[c]
Oxygen	O	8	15.999	2	6				6+	2,(1)[d]
Fluorine	F	9	18.998	2	7				7+	1
Neon	Ne	10		2	8				0	
Phosphorus	P	15	30.974	2	8	5			5+	3,5
Sulfur	S	16	32.06	2	8	6			6+	2,4,6(1)[d]
Chlorine	Cl	17	35.453	2	8	7			7+	1
Argon	Ar	18		2	8	8			0	
Bromine	Br	35	79.904	2	8	18	7		7+	1
Krypton	Kr	36		2	8	18	8		0	
Iodine	I	53	126.905	2	8	18	18	7	7+	1
Xenon	Xe	54		2	8	18	18	8	0	

*From Schwarzenbach et al. 1993

[a] The underlined elements are the noble gases.

[b] Based on the assigned atomic mass of $^{12}C = 12.000$ amu; abundance-averaged values of the naturally occurring isotopes.

[c] Positively charged atom.

[d] Negatively charged atom.

Before 1926, two types of bonds were thought to exist: ionic and covalent. These were based on the concept that an atom reaches the greatest stability when the center (or outer shell of electrons) is full. Both ionic and covalent bonds arise in the "attempt" to attain a stable configuration.

A general definition of an ionic bond is one formed when the electrostatic attraction between oppositely charged ions holds them together. A covalent bond is formed when each atom shares electrons to fill the shell. Here too, the binding force is electrostatic attraction, this time between each electron and *both* nuclei. The bond

reflects a balance between this attraction and the repulsion of the nuclei towards each other.

The theories of quantum mechanics, introduced in 1926, changed this fundamental concept of chemical bonds. Instead of thinking about an electron existing at a fixed location, the motion of an electron is described in terms of its energy. The equation describing the motion of electrons tells us the probability of finding the electron at any particular place. In quantum mechanics the region in space where an electron is most likely to be found is an *orbital*. *Localized* chemical bonding is defined as bonding in which the electrons are shared by two and only two nuclei. In *delocalized* bonding, electrons are shared by more than two nuclei.

For a covalent bond to form, two atoms must be located so that the orbital of one overlaps the orbital of another and each orbital must contain a single electron. This overlap arrangement of electrons and nuclei contains less energy than the isolated atoms. The amount of energy that is liberated when a bond is formed (or required to break the bond) is called the *bond dissociation energy*. Bond dissociation energies can vary widely from weaker bonds, such as $CH_3 - I$ (56 kcal/mole) to stronger bonds such as $C_6H_5 - H$ (112 kcal/mole). For a list of bond dissociation energies see Table 8.2.

Table 8.2 Average Bond Lenghts (Å) and average Bond Enthalpies ($kJ \cdot mol^{-2}$) of Some Important Covalent Bonds*

| Bond	Length/Enthalpy	Bond	Length/Enthalpy	Bond	Length/Enthalpy
		Diatomic Molecules			
H—H	0.74/436	F—F	1.42/155	O=O	1.21/498
H—F	0.92/566	Cl—Cl	1.99/243	N≡N	1.10/946
H—Cl	1.27/432	Br—Br	2.28/193		
H—Br	1.41/367	I—I	2.67/152		
H—I	1.60/298				
		Covalent Bonds in Organic Molecules			
Single Bonds					
H—C	1.11/415	C—C	1.54/348	C—F	1.38/486
H—N	1.00/390	C—N	1.47/306	C—Cl	1.78/339
H—O	0.96/465	C—O	1.41/360	C—Br	1.94/281
H—S	1.33/348	C—S	1.81/275	C—I	2.14/216
Double and triple bonds					
C=C	1.34/612	C=O [d]	1.20/737	C≡C	1.20/838
C=N	1.28/608	C=O [e]	1.20/750	C≡N	1.16/888
C=S [c]	1.56/536	C=O [f]	1.16/804		

*Schwarzenbach et al. 1993

[a] Bond length/bond enthalpy. Note that 1Å equals 0.1nm.

[b] Bond lengths are given for bonds in which none of the partner atoms is involved in a double or triple bond. In such cases bond lengths are somewhat shorter.

[c] In carbon disulfide. [d] In aldehydes. [e] In ketones. [f] In carbon dioxide.

Having a general idea about the energy involved in holding atoms together in covalent bonds will help us evaluate the strengths of other interactions. The bond dissociation enthalpy (ΔH_{AB}) is defined as the heat change of the gas phase reaction:

$$AB \rightarrow A^{\cdot} + B^{\cdot}$$
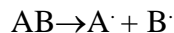
at constant temperature and pressure (25 $^{\circ}$C, 1 atm.) These are indirectly determined for each bond in a molecule by thermochemical studies of evolved heat (calorimetric measurements) and data analysis. But generally they are presented as average enthalpy for a particular bond type (and are a proxy for bond strength).

There are a few important trends to note. Note that bond lengths of the first row elements (C, N, O, F) with H are all around 1 Å. When one compares the strength of double bonds and single bonds; double bonds are stronger than single bonds, but are not as strong as two single bonds. Another important trend is relative strengths of the H-H bond versus the H-halogen bonds. Note that the H-F has the highest enthalpy and shortest length of the series. From this we can see that there must be an uneven distribution of electrons in a chemical bond, this is the concept of *electronegativity*.

Electronegativity

Generally the electron cloud that bonds two atoms is not symmetrical (with respect to the plane that is the perpendicular bisector of the bond) except for two identical atoms (e.g. H-H) and they have the same substituents. The cloud is distorted towards one side of the bond, depending on which atom has a stronger attraction for the cloud, that is towards the more *electronegative* atom. This results in accumulation of negative charge towards one end of the bond, denoted as δ-; the deficiency at the other end is denoted δ+.

$$\overset{|}{\underset{|}{-C^{\delta+}}}-X^{\delta-}$$
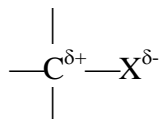
Based on the trends of the H-halogen bonds, one might hypothesize that the smaller the atom and the higher the net charge of the kernel (nucleus plus the electrons of the inner filled shells) the more electronegative the atom. There have been many scales devised to indicate the size and distortion of the electron cloud a bond between any two atoms. Pauling devised the most widely used of these scales. It is based on bond energies of diatomic molecules, comparing the actual bond energy to the energy if the electrons were equally shared. To develop this, it was necessary to assign a value to one element arbitrarily (F = 4.0). The scale is presented below (Table 8.3) presented as a function of net charge of the kernel.

When the differences in electronegativities is great, the orbital may be so far over to one side that it barely covers the other nucleus. This is an *ionic bond*, leaving us with one type of bond. Basically most bonds are considered intermediate between ionic and covalent. For this review we will use the term ionic and covalent bonds, with the understanding that they represent two extremes of electron cloud distribution.

Bonds with partial ionic character are often referred to as *polar* covalent bonds. These arise due to the charge separation involving bonds between atoms with different electronegativities. The partial charge separation makes each bond between dissimilar atoms a *dipole*. The *dipole moment* is a property of a molecule. Because of the small differences in electronegativities of carbon and hydrogen, alkanes have very small dipole moments (<1 D (Debye, 1 D is equivalent to the separation of 2 point charges of opposite sign, a distance of 10^{-8} cm, 1 D = 3.336 x 10^{-30} C m).) Some substituent groups (e.g. nitro (NO_2-), hydroxy (OH-) or halogens) cause a greater dipole moment. Few organic molecules dipole have moments above 7 D. Some molecules, because of their symmentry have no dipole moments.

Table 8.3. Electronegativities of Atoms According to the Scale Devised by Pauling (1960)*

Charge of kernel:	+1	+4	+5	+6	+7	
	H 2.2					Increasing size of kernel ↓
		C 2.5	N 3.0	O 3.5	F 4.0	
			P 2.2	S 2.5	Cl 3.0	
					Br 2.8	
					I 2.5	

*Schwarzenbach et al. 1993

The dipole bond moments of O-H, N-H and F-H are unusually large (1.51, 1.31, 1.94 D, respectively). Since the electron-depleted H atom is also very small, other electronegative atoms, e.g., -O, -N, and –F can get quite close to the polar X-H groups and thus experience a strong field. This results in a strong attractive force that can align neighboring molecules possessing such groups in both the liquid and crystalline state. The special type of interaction is known as *hydrogen bonding*.

Hydrogen bonding is conventionally regarded as being limited to N, O, and F, but if some anionic species (such as Cl⁻), it may also participate in hydrogen bonding. The hydrogen 'bonds' (electrostatic in character) are special in that they only involve hydrogen atoms, which by virtue of their tendency to become positively polarized and their uniquely small size, can interact strongly with nearby electronegative atoms resulting in an effective H-mediated 'bond' between two electronegative atoms.

If the electron-rich center and the hydrogen are in the same molecule, this is known as *intra*molecular hydrogen bond. If it is between different molecules, it is referred to as an *inter*molecular hydrogen bond. The strength of hydrogen bonds lie between 10 and 40 kJ mole⁻¹, which makes them stronger than a typical van der Waals "bond" (about 1 KJ mole⁻¹) but still much weaker than covalent or ionic bonds (about 500 KJ mole⁻¹.) Hydrogen bonds can exist in a non-polar environment.

There must be forces between nonpolar compounds, such attraction is called *van der Waals* forces. In a nonpolar molecule, the average distribution of charge is

symmetrical, so there is no net dipole moment. However, electrons move about, so at any instant in time, the cloud is distorted and a small dipole will exist. The momentary dipole will affect the electron distribution in a neighboring molecule. The negative end of the dipole will tend to repel electrons, the positive end will attract them, *inducing* a dipole. The momentary dipoles and the induced dipoles are constantly changing and the result is an attraction between molecules. These van der Waal forces are the weakest intermolecular forces and have very short range.

Many of the organic chemicals are relatively stable in the environment. This is due primarily to the high energy barrier to break bonds, not that that the atoms are in their lowest enery states. Thus organic molecules are stable for kinetic, not thermodynamic reasons. If energy is provided to overcome the activation energy (e.g. a flame to methane or UV irradiation to chlorofluorocarbons), then the reaction will process. Reactions that release energy (denoted by an overall negative ΔH (heat of reaction) are called *exothermic* reactions. If there is a positive ΔH, it implies the reaction consumes heat by taking energy into the product structures; these are called *endothermic* reactions.

Many reactions (e.g. combustion) the reactant has non-polar bonds and the product have polar bonds. In this process electrons are transferred from one chemical species to another. We refer to these reactions as *redox* reactions. Generally when determining the oxidation state of an atom in a molecule, one can formally assign the possession of an electron pair to the more electronegative atom. Thus the oxidation state may be computed by adding 0 for each bond to an identical atom, -1 for each bond to a more electronegative atom (or negative charge) and +1 for each bond to a less electronegative atom (or a positive charge.) For example the oxidation state for the carbon in methane is -4 C(-IV) and for the hydrogen is +1; for CO_2 the oxidation state for carbon is +4 C(IV)and for O is –2. Note that Roman instead of Arabic numbers are used to express oxidation state.

Spatial Arrangements

A simple rule to remember when looking at bond angles is that each pair of electrons wants to stay as far as possible away from another pair. That means that C, which can form 4 bonds, the bonds will generally point to the corners of a tetrahedral. The exact tetrahedral angle ($109^o28'$) will only occur if all the substituent groups are identical. In most cases the angle deviate from the pure tetrahedral value. For *saturated* carbon atoms (carbon atoms not involved in double or triple bonds), the C-C-C angles are typically 112° (except for ring systems).

The association of electrons in a single (or sigma, σ) bond does not prevent rotation around the axis of linkage.   Some of these molecules, however, do exhibit *stereoisomerism;* stereoisomers are compounds with the same atoms and bonds, but having different three-dimensional structures. One example of this is *chirality.* A molecule is called chiral if the image and mirror image are distinguishable. Non-identical, mirror image molecules (e.g. tartaric acid) are called *enantiomers.* Although they differ only from each other in the way the atoms are oriented in space, they can have vastly different reactivities. Many compounds are biologically active, although their enantiomers are not. If there is more than one assymmetrical center in the compound, it

is called a *diastereomer*. Diastereomers are not mirror images of each other. Chirality is a necessary and sufficient condition for the existence of enantiomerism.

An important form of diastereomerism results from the restricted rotation about double or triple bonds and/or ring structures. One bond (the sigma bond) occupies the volume in between the two atoms. For double bonds, the second bond (the pi (π) bond) is an electron cloud above and below the plane of the other bond (or non-bonded electrons). For triple bonds, the two π-bond electron clouds are orthogonal to each other, leading to a linear (180°) bonding configuration.

Since rotation is restricted around these bonds, isomerism occurs. To distinguish between the two isomers, one commonly uses the terms *cis* and *trans* to describe the positions of the two substituent groups (each bound to one atom of the double bond). Cis refers to if the two substituents are on the same side of the double bond. Trans compounds have the substituents on opposite sides of the double bond. These isomers can exhibit quite different properties. For example *trans*-dichloroethene has a boiling point of 48 $^{\circ}$C vs 60 $^{\circ}$C for *cis*- dichloroethene:
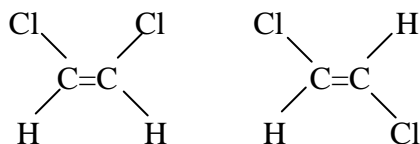
cis   trans

This same terminology can be applied to ring compounds if there are two substituents on the ring. In ring systems with more than two substituted carbons, Greek letters are used to identify the isomers (α, β and γ). Different isomers can have vastly different reactivities and biological activity.

Delocalized Chemical Bonding

Many compounds contain one or more bonding orbitals that are not restricted to two atoms, but are spread out over three or more. Such bonding is called *delocalized*. Energetically, not constraining the electrons to two atoms, lowers the energy (and stabilizes the molecule.) There are three main type of structures that exhibit resonance: (1) double or triple bonds in conjugation (adjacent to each other). Benzene is the classical example of this. Butadienne, a linear molecule, is also a good example. These structures are thought to contribute to resonance:

$$CH_2=CH-CH=CH_2 \leftrightarrow \overset{+}{C}H_2-CH=CH-\overset{-}{C}H_2 \leftrightarrow \overset{+}{C}H_2=CH-\overset{-}{C}H-CH_2$$

(2) double or triple bonds in conjugation with a with a p orbital on an adjacent atom. This is a case where three parallel p orbitals overlap, forming molecular orbitals. A typical example is vinyl chloride:

$$CH_2=CH\text{-}Cl \leftrightarrow CH_2\overset{-}{}\text{-}CH=\overset{+}{Cl}$$
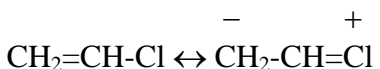
Any system with an atom that has an unshared pair of electrons and is directly attached to a multiple bond atom can show this type of delocalization.

(3) hyperconjugation, the third type of delocalization involves σ electrons. This type of resonance is called no-bond resonance and is important for carbocations and free radicals. It will not be discussed.

Acids and Bases

  An acid, according to Lowry-Bronsted, is a substance that gives up a proton. A base is a substance that accepts a proton. According to this definition, the "strength" of an acid depends on its tendency to give up a proton, the strength of a base on its tendency to accept a proton.

$$\text{Acid Strength } H_2SO_4, HCl > H_3O^+ > NH_4^{+} > H_2O$$

$$\text{Base Strength } HSO_4^+, Cl^- < H_2O < NH_3 < OH^-$$
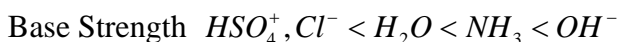
Many organic chemicals that contain oxygens or nitrogens can act as base and accept protons.

  Another definition of an acid and base which is more fundamental to the understanding or organic chemistry is the Lewis definition. According to the Lewis definition: An acid is an electron-pair acceptor (i.e., it accepts an electron pair to form a covalent bond) and a base is an electron pair donor (i.e., it gives up an electron pair to form a covalent bond). To be acidic in the Lewis sense, a molecule must be electron deficient. One such acid would be an oxygen atom bearing only a sextet of electrons.

8.2 Compound Groupings

Hydrocarbons can be broken into two groups: aliphatics and aromatics. The original meaning of the words "aliphatic" (fatty) and "aromatic" (fragrant) no longer have any significance. Aliphatic compounds are open-chain compounds and those cyclic compounds that resemble open-chain compounds. Aromatic compounds are benzene and compounds that resemble benzene in chemical behavior.

Figure 8.1: Hydrocarbon Families
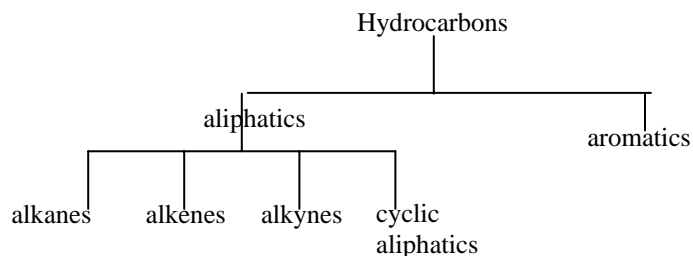
Aliphatic Hydrocarbons

Alkanes

Alkanes are hydrocarbons in which each carbon atom has four covalent bonds. Methane is the simplest member of the alkanes family, with a single carbon with four covalent bonds to hydrogens.

Methane is a non-polar molecule. It is not very reactive, reacting with only highly reactive substances. Some reactions of methane are oxidation and chlorination.

Oxidation:

$$CH_4 + O_2 \overset{flame}{\leftrightarrow} CO_2 + 2H_2O + \text{ heat}$$

$$CH_4 + O_2 \overset{heat}{\leftrightarrow} \text{ variety of polar products}$$
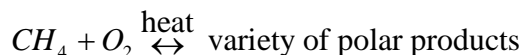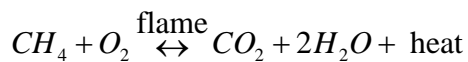
Chlorination (a substitution reaction):

$$CH_4 \xrightarrow[Cl_2]{HCl} CH_3Cl \xrightarrow[Cl_2]{HCl} CH_2Cl_2 \xrightarrow[Cl_2]{HCl} CHCl_3 \xrightarrow[Cl_2]{HCl} CCl_4 \quad \text{(heat or light required)}$$
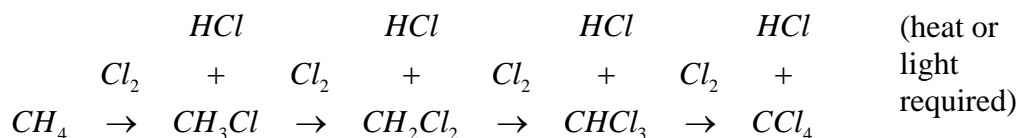
Alkanes containing a higher number of carbons can form straight chain or branched chain groups. The longer the carbon chain becomes, the more configurations an alkane group can have. Some examples of the longer chain compounds are as follows:

ETHANE (can rotate around C-C bond to form conformations)
$\left(C_2H_6\right)$

```
        H       H
        |       |
H ——  C  ——  C  —— H
        |       |
        H       H
```

PROPANE
$\left(C_2H_8\right)$

```
        H      H      H
        |      |      |
H—  C  —   C—  C  —H
        |      |      |
        H      H      H
```
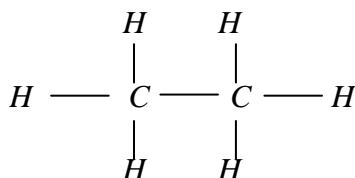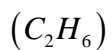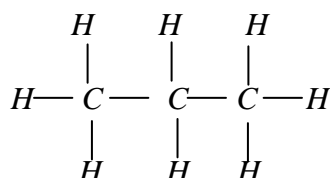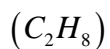
BUTANE (can branch to form isomers)
$\left(C_4H_2O\right)$

```
   H    H    H    H                          H       H       H
   |    |    |    |                          |       |       |
H— C —  C —  C —  C  —H            H ——  C  ——  C  ——  C  —— H
   |    |    |    |                          |       |       |
   H    H    H    H                          H    H— C —H    H
                                                     |
                                                     H
```
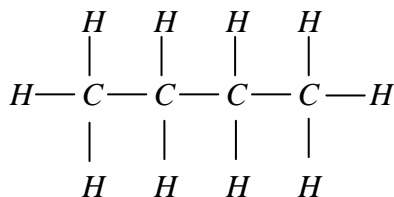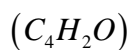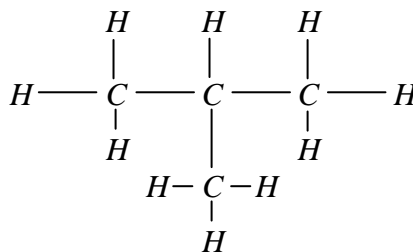
        n-butane   isobutane
                                   (a one carbon "branch")

PENTANE (C_5H_{12} three isomers)

HEXANE (C_6H_{14} five isomers)

Nomenclature of these compounds is as follows.

        Straight chain alkanes:

CH_4	methane
C_2H_6	ethane
C_3H_8	propane
C_4H_{10}	butane

C_5H_{12} pentane

C_6H_{14} hexane

C_7H_{16} heptane

C_8H_{18} octane

Alkyl groups:

CH_3, methyl (e.g., methyl chloride CH_3Cl)

C_2H_5, ethyl (e.g., ethyl chloride C_2H_5Cl)

etc.

Branched chains:

Name the compound by the longest chain, number the carbon where the branch occurs:
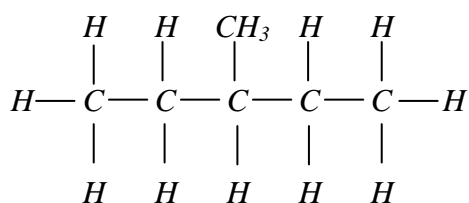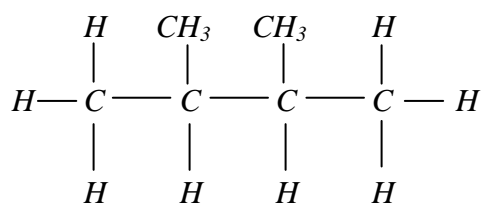
3-methyl pentane   2,3-dimethyl butane

Physical Properties

Alkanes are non-polar molecules. Physical properties (such as melting point, boiling point, etc.) change with increasing chain length. This is because the intermolecular forces increase with chain length (e.g., boiling points and melting points increase). Alkanes are soluble in non-polar solvents (benzene, ether, chloroform). They are less dense than water. If, however, a heavier atom, such as chlorine, is substituted for hydrogen, the substituted alkane can be denser than water.

Alkenes

Alkenes contain less hydrogen, carbon for carbon, than alkanes, and can be converted into alkanes by addition of hydrogen. These are referred to as "unsaturated" compounds, i.e., they contain less than the maximum quantity of hydrogen. The unsaturated carbons have "carbon-carbon double" bonds.

The simplest alkene is ethene, a two-carbon chain. The number of isomers per length of the carbon chain increases more rapidly for alkenes than for alkanes as rotation

around the double bond increases the number of isomers. Some examples of alkenes follow:

ETHYLENE OR ETHENE
(C_2H_4)

$$
\begin{array}{ccc}
H & & H \\
\diagdown & & \diagup \\
C & = & C \\
\diagup & & \diagdown \\
H & & H
\end{array}
$$

PROPYLENE OR PROPENE
(C_3H_6)

$$
\begin{array}{ccccccc}
 & H & & H & & H & \\
 & | & & | & & | & \\
H\!-\!\!\!-\! & C & \!-\!\!\!-\! & C & = & C & \!-\!\!\!-\!H \\
 & | & & & & & \\
 & H & & & & &
\end{array}
$$
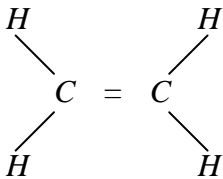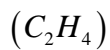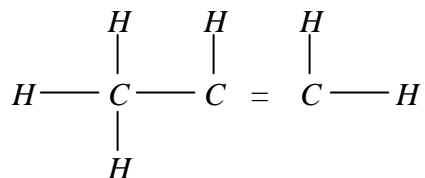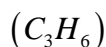
BUTYLENE OR BUTENE (four isomers)
(C_4H_8)

$$
\begin{array}{ccccccccc}
 & H & H & & H & H & & & \\
 & | & | & & | & | & & & \\
H\!-\! & C & =\!C & \!-\! & C & \!-\!C & \!-\!H & & \\
 & & & & | & | & & & \\
 & & & & H & H & & &
\end{array}
$$
1-butene

$$
\begin{array}{ccc}
H & & CH_3 \\
\diagdown & & \diagup \\
& C = C & \\
\diagup & & \diagdown \\
CH_3 & & H
\end{array}
$$
trans-2-butene

$$
\begin{array}{ccccc}
H & & & & H \\
| & & & & | \\
H\!-\!C & \!-\! & C & =\!C & \!-\!H \\
| & & | & & \\
H & & CH_3 & &
\end{array}
$$
isobutene
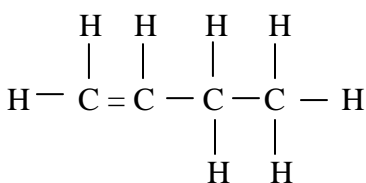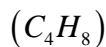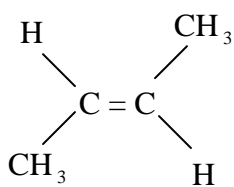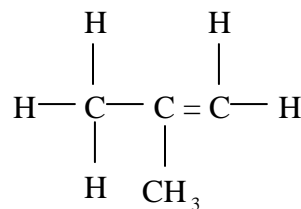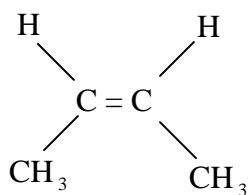
$$
\begin{array}{ccc}
H & & H \\
\diagdown & & \diagup \\
& C = C & \\
\diagup & & \diagdown \\
CH_3 & & CH_3
\end{array}
$$
cis-2-butene

The nomenclature for alkenes is similar to that for alkanes, except that names end in -ene instead of -ane and the number in front of the name specifies the carbon of the double bond which is closest to the end. Some examples are as follows:

$$CH_2 = CH_2 \qquad\qquad CH_3 - CH = CH_2 \qquad\qquad CH_3CH_2CH = CH_2$$
  ethylene   propene   1-butene

$$CH_3CH = CHCH_3 \qquad\qquad \overset{\displaystyle CH_2}{\underset{}{\overset{|}{CH_3 - C = CH_2}}}$$

2-butene (cis or trans)   2-methylpropene

$$CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH = CH_2 \qquad\qquad CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - CH = CH - CH_3$$

3,3-dimethyl-1-butene   4-methyl-2-pentene
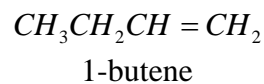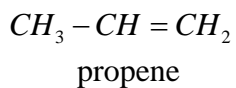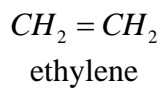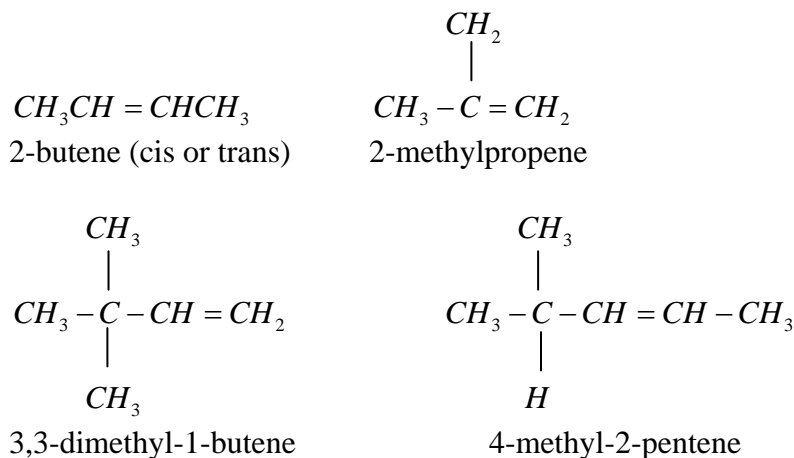
Physical Properties

The physical properties of alkenes are similar to alkanes. They are insoluble in water. The boiling point and melting point rises with length of chain. Alkenes are "slightly" more polar than alkanes.

Substituting more electronegative atoms (e.g. halides) for hydrogens can give the molecule a dipole moment, changing the physical properties, such as increasing the boiling point. See Table 8.4 for the physical properties.

Table 8.4 Physical Properties of Alkanes

Name	Formula	M.p., °C	B.p., °C	Density (at 20°)
Methane	CH_4	-183	-162	
Ethane	CH_3CH_3	-172	- 88.5	
Propane	$CH_3CH_2CH_3$	-187	- 42	
n-Butane	$CH_3(CH_2)_2 CH_3$	-138	0	
n-Pentane	$CH_3(CH_2)_3 CH_3$	-130	36	0.626
n-Hexane	$CH_3(CH_2)_4 CH_3$	- 95	69	.659
n-Heptane	$CH_3(CH_2)_5 CH_3$	- 90.5	98	.684
n-Octane	$CH_3(CH_2)_6 CH_3$	- 57	126	.703
n-Nonane	$CH_3(CH_2)_7 CH_3$	- 54	151	.718
n-Decane	$CH_3(CH_2)_8 CH_3$	- 30	174	.730
n-Undecane	$CH_3(CH_2)_9 CH_3$	- 26	196	.740
n-Dodecane	$CH_3(CH_2)_{10} CH_3$	- 10	216	.749
n-Tridecane	$CH_3(CH_2)_{11} CH_3$	- 6	234	.757

n-Tetradecane	$CH_3(CH_2)_{12}CH_3$	5.5	252	.764
n-Pentadecane	$CH_3(CH_2)_{13}CH_3$	10	266	.769
n-Hexadecane	$CH_3(CH_2)_{14}CH_3$	18	280	.775
n-Heptadecane	$CH_3(CH_2)_{15}CH_3$	22	292	
n-Octadecane	$CH_3(CH_2)_{16}CH_3$	28	308	
n-Nonadecane	$CH_3(CH_2)_{17}CH_3$	32	320	
n-Eicosane	$CH_3(CH_2)_{18}CH_3$	36		
Isobutane	$(CH_3)_2CHCH_3$	-159	- 12	
Isopentane	$(CH_3)_2CHCH_2CH_3$	-160	28	.620
Neopentane	$(CH_3)_4C$	- 17	9.5	
Isohexane	$(CH_3)_2CH(CH_2)_2CH_3$	-154	60	.654
3-Methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$	-118	63	.676
2,2-Dimethylbutane	$(CH_3)_3CCH_2CH_3$	- 98	50	.649
2,3-Dimethylbutane	$(CH_3)_2CHCH(CH_3)_2$	-129	58	.668

Dienes

Dienes are simply alkenes that contain two carbon-carbon double bonds. Molecules that contain three double bonds are called trienes. The nomenclature for dienes and trienes is similar to alkenes, specifying the number of the carbons of the double bonds that are closest to the end of the chain. Names of dienes end in -diene, and the trienes end in -triene. Some examples of dienes and trienes are as follows.

$$CH_2 = CH - CH = CH_2 \qquad\qquad CH_2 = CH - CH_2 - CH = CH_2$$
$$\text{1,3-butadiene} \qquad\qquad\qquad\qquad \text{1,4-pentadiene}$$

$$CH_2 = CH - CH = CH - CH = CH_2$$
$$\text{1,3,5-hexatriene}$$
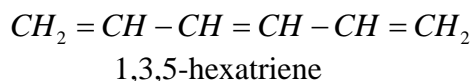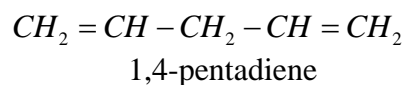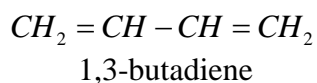
Double bonds which alternate with single bonds are said to be conjugated (have delocalized electrons); double bonds which are isolated by more than a single bond are said to be isolated. A third class of dienes, called allenes, contain accumulated double bonds.

$$-\overset{|}{C} = C = \overset{|}{C} -$$
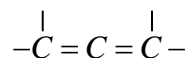
Conjugated dienes tend to be more stable than isolated dienes. They are, however, much more reactive than ordinary alkenes.

Alkynes

Alkynes display an even higher degree of unsaturation than alkenes. They have the general formula $C_nH_{2_{n-2}}$. The outstanding feature of this group is the formation of a triple bond between two carbons. The simplest alkyne is ethyne or acetylene. The alkynes are names similarly to the alkanes and alkenes, except with an -yne ending, for example:

$$HC \equiv C - C_2H_5 \qquad\qquad CH_3 - C \equiv C - CH_3 \qquad\qquad CH_3 - C \equiv C - CH\left(CH_3\right)_2$$

<div align="center">
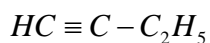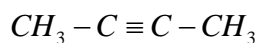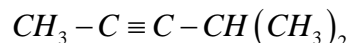
1-butyne   2-butyne   4-methyl-2-pentyne

</div>

Physical Properties

These are low polarity compounds. They are insoluble in water, soluble in organic solvents of low polarity (e.g., ligroin, ether, benzene, and carbon tetrachloride). Boiling points and melting points show the same trend as alkenes and alkanes.

Cyclic Aliphatic Hydrocarbons

Up to now we have talked about open-chain compounds, i.e., carbons attached on one another to form chains. In many compounds they are arranged as rings; these arecalled cyclic compounds.

The nomenclature for these compounds is similar to the open chain compounds, except that the prefix of cyclo- is added to the name of the corresponding open-chain hydrocarbon. Some examples of cyclic hydrocarbons are as follows.
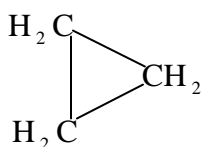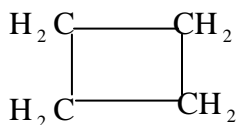
Cyclopropane   Cyclobutane   Cyclopentene
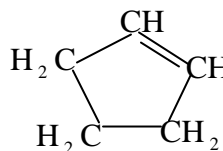
1,3-Dimethyleyelohexane   1,3-Cyclohexadiene

In drawing these structures, it is usually understood that two hydrogens are located at each corner unless another group is indicated. Typically 5- and 6-membered rings are the most stable.
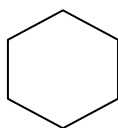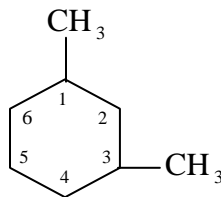
Chlorocyclopropane
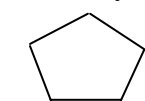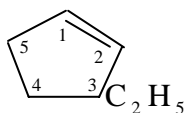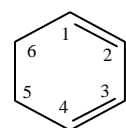
Cyclopentane

3-Ethylcyclopentene
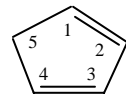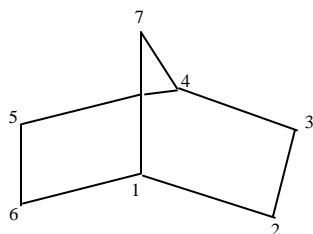
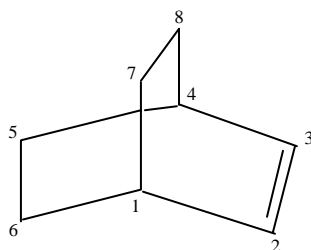1,3-Cyclopentadiene

Cyclohexane

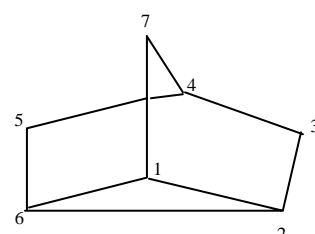1,3-Dimethylcyclohexane

1,3-Cyclohexadiene

Polycyclic compounds contain two or more rings that share two or more carbon atoms, for example:

Bicyclo[2.2.1]heptane
Norbornane

Bicyclo[2.2.2]octa-2-ene

Tricyclo[2.2.1.0$^{2.6}$]heptane
Nortricyclene

Physical Properties

Physical properties for cyclic aliphatics follow the same trends as the straight chain aliphatics.

Aromatic Hydrocarbons (or Arenes)

Aromatic compounds are compounds that resemble benzene in chemical behavior. These compounds have certain distinctive chemical properties. It is, however, important not to attach undue weight to the distribution between aromatics and aliphatics, as subgroups in these two groups might behave similarly, e.g., aliphatic and aromatic acids.
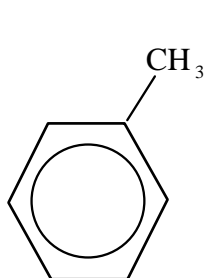
Benzene

Benzene $\left(C_6H_6\right)$ is a highly symmetrical molecule, in which each hydrogen is assumed to be equivalent.
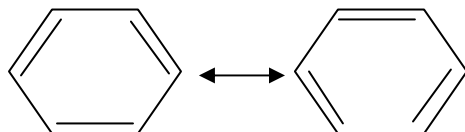

In benzene, it is assumed that the electrons are "delocalized" or in "resonance". As we discussed in covalent bonding, association with a pair of electrons with two nuclei results in stabilization in the formation of a localized bond; association with more than two nuclei would lead to greater stabilization and delocalized bonds. This is proposed for benzene.
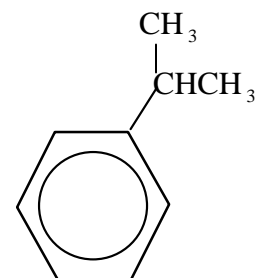
More complex aromatics consists of substituted benzenes (benzene derivaties) and polycyclic compounds. Some of the more common benzene derivatives are given below.
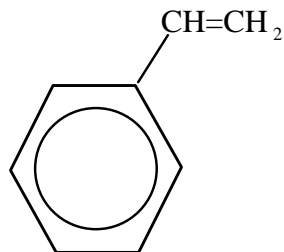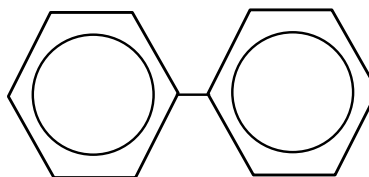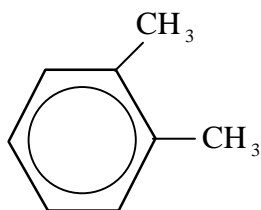

toluene
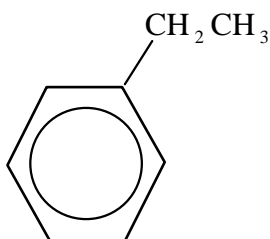
ethylbenzene

cumene
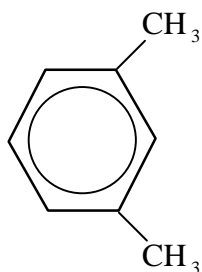(isopropylbenzene)

styrene
(vinylbenzene)

biphenyl
(phenylbenzene)

Each of these compounds is named as an alkyl, alkenyl or aryl benzene (unless a "trivial" name, such as toluene is used). The hydrocarbon group (C_6H_5-) is known as a phenyl group.
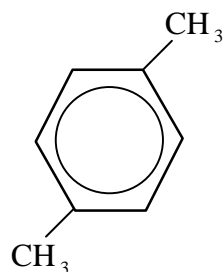
When two or more substitutions occur on a benzene ring, isomerization ocurrs. These isomers arise because the substitutes can have a 1,2, 1,3 or 1,4 relationship (or ortho, meta, and para, or *o*, *m*, and *p* relationship). For example:
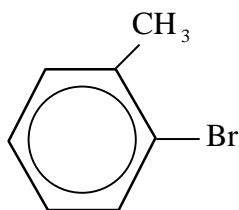

ortho-xylene (1,2-dimethylbenzene o-xylene)	meta-xylene (1,3-dimethylbenzene m-xylene)	para-xylene (1,4-dimethylbenzene p-xylene)
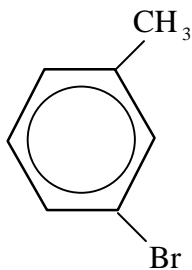
o-bromotoluene	m-bromotoluene	p-bromotoluene
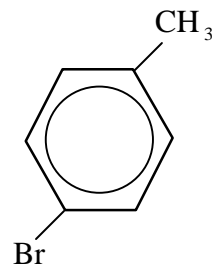
Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons (or PAHs) have more than one benzene ring and share common carbon atoms. They are formed whenever organic substances are exposed to high temperatures (such as in incinerators). PAHs will form a lower temperatures, but the times of reaction is quite long. The PAHs in oil took millions of years under certain conditions (temperature and pressure) to form.

Nomenclature

A wide range of PAHs have benzene rings with common "ortho" positions. Three important examples are:
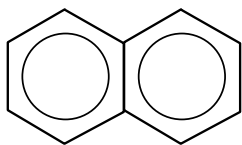
| naphthalene | anthracene | phenanthrene |

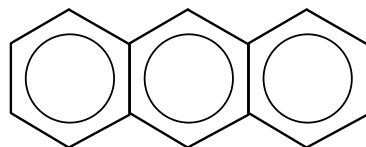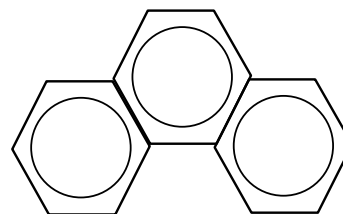Mono substitutions products are named either using numbers or Greek letters. Some examples:
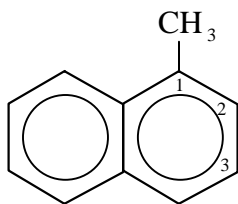
1-methylnaphthalene
χ-methylnaphthalene
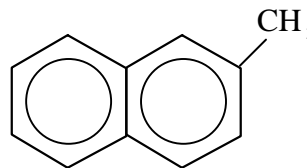
2-methylnaphthalene
ρ-methylnaphthalene

Many polycyclic aromatic hydrocarbons have been given names that are uniformative of the structure. An extra ring, which adds only four carbons at most, is designated by the prefix benzo (or benz - if followed by a vowel).

Benzo[a]pyrene (B[a]p) is a compound of interest as the unit cancer risk calculated for this compound has been used by the U.S. EPA as a surrogate for all polycyclic aromatic hydrocarbons. (See Figure 8.2).

Figure 8.2: Example for Nomenclature of PAH
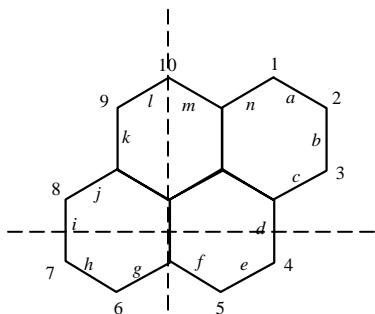
Pyrene
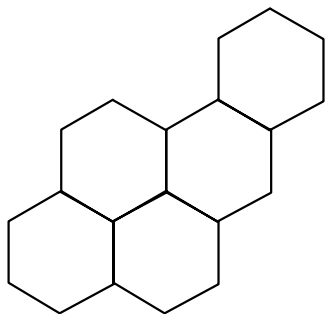
Benzo (a) Pyrene
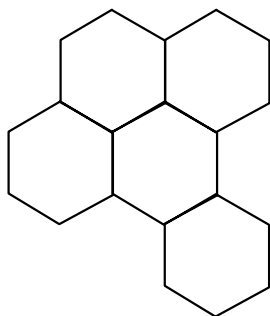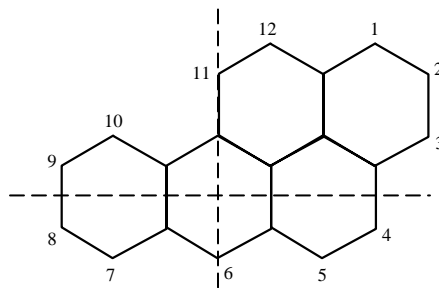
Benzo (e) Pyrene
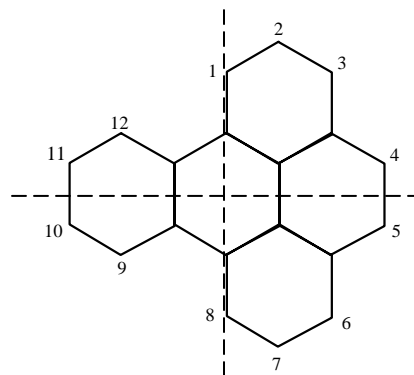
Physical Properties

Many derivatives of arenes have pleasant odors (hence the name aromatics). The arenes themselves are generally quite toxic. Some of them can induce cancer or cause mutations at very low concentrations (for example, B[a]p).

They are less dense than water and highly insoluble. Boiling points increase with molecular weight. Benzene is the least reactive of the arenes. PAHs are slightly more reactive as the carbon hydrogen bonds are not all equal in strength. The delocalized nature of the electrons in these aromatic compounds helps to make these structures more stable than their open-chain precursors.

Substituted Hydrocarbons

Up to this point we have talked about the different classifications of hydrocarbons: aliphatics (alkanes, alkenes, alkynes and cyclic aliphatic compounds), and aromatics and some of their key physical properties. We will now discuss physical properties of substituted hydrocarbons.

The hydrogens on hydrocarbons can be replaced with functional groups. These groups can be different hydrocarbons (for example, an alkyl group) or can be groups which contain other elements: e.g., *O, N, P, S, Cl, Br, I* or *F*. These substituted hydrocarbons can be classified by the hydrocarbon group, or, another classification scheme of organic compounds considers them as substitution products of water, ammonia, hydrogen sulfide, nitrous or nitric acids, and so on. This classification scheme is illustrated in Table 8.5.

Table 8.5 Organic Compounds as Derivatives of Common Inorganic Compounds

parent compound	organic derivative			
	class of compound		example	
$H-O-H$	$R-O-H$	alcohol	CH_3OH	methanol
	$R-O-R'$	ether	CH_3OCH_3	dimethyl ether
	$R-\overset{\overset{O}{\parallel}}{C}-O-H$	carboxylic acid	$CH_3\overset{\overset{O}{\parallel}}{C}OH$	acetic acid
	$R-\overset{\overset{O}{\parallel}}{C}-O-R'$	carboxylic ester	$CH_3\overset{\overset{O}{\parallel}}{C}OCH_3$	methyl acetate
	$R-\overset{\overset{O}{\parallel}}{C}-O-\overset{\overset{O}{\parallel}}{C}-R$	carboxylic anhydride	$CH_3\overset{\overset{O}{\parallel}}{C}O\overset{\overset{O}{\parallel}}{C}CH_3$	acetic anhydride
$H-S-H$	$R-S-H$	thiol (mercaptan)	CH_3SH	methanethiol (methyl mercaptan)
	$R-S-R'$	thioether (sulfide)	CH_3SCH_3	methylthiomethane (dimethyl sulfide)
	$R-\overset{\overset{O}{\parallel}}{C}-S-H$	thio acid	$CH_3\overset{\overset{O}{\parallel}}{C}SH$	thioacetic acid
NH_3	RNH_2	*prim.* amine	CH_3NH_2	methylamine
	R_2NH	*sec.* amine	$(CH_3)_2NH$	dimethylamine
	R_3N	*tert.* amine	$(CH_3)_3N$	trimethylamine
	$R-\overset{\overset{O}{\parallel}}{C}-NH_2$	acylamine (unsubstituted amide)	$CH_3-\overset{\overset{O}{\parallel}}{C}-NH_2$	acetamide
	$R-\overset{\overset{O}{\parallel}}{C}-NHR$	(monosubstituted amide)	$CH_3-\overset{\overset{O}{\parallel}}{C}-NHCH_2$	N-methyl-acetamide
	$R-\overset{\overset{O}{\parallel}}{C}-NR_2$	(disubstituted amide)	$CH_3-\overset{\overset{O}{\parallel}}{C}-N(CH_3)_2$	N,N-dimethyl-acetamide
$H-ONO_2$ (nitric acid)	$R-ONO_2$	alkyl nitrate	CH_3-ONO_2	methyl nitrate
$H-ONO$ (nitrous acid)	$R-ONO$	alkyl nitrite	CH_3-ONO	methyl nitrite
$H-NO_2$ (unknown)	$R-NO_2$	nitroalkane	CH_3-NO_2	nitromethane

Table 8.5 Organic Compounds as Derivatives of Common Inorganic Compounds (continued)

parent compound	organic derivative			
	class of compound		example	
$H-NO$ (hypo-nitrous acid, monometic form)	$R-NO$	nitrosoalkane	CH_3-NO	nitrosomethane
$H-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH$ (sulfuric acid)	$R-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH$	alkyl hydrogen sulfate	$CH_3-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH$	methyl hydrogen sulfate
	$R-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-O-R$	dialkyl sulfate	$CH_3-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OCH_3$	dimethyl sulfate
$H-X$ $\left(X=F,Cl,Br,I\right)$	$R-X$	alkyl halide (haloalkane)	CH_3-F	methyl fluoride (fluoro-methane)

Nomenclature

Alcohols: -ol is appended to name of parent hydrocarbon, or (similar to alkyl halides), the name of the appropriate alkyl group is combined with the work alcohol (or halide).

$$CH_3 - CH_2 - CH_2 - OH$$
propyl   alcohol
propanol
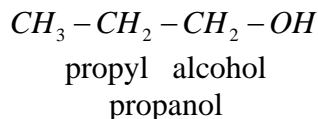
Ethers: named as dialkyl, dialkenyl or diaryl ethers

$$CH_3CH_2 - O - CH_2CH_3$$
diethyl ether
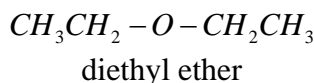
Carboxylic Acids: saturated alkyl chains are named alkanoic acids. (Many trivial names exist for common carboxylic acids.)

$$Cl$$
$$|$$
$$CH_3CH_2CH_2CHCO_2H$$
2-chloropentanoic acid
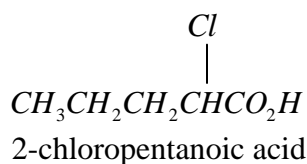
Common names:

HCO_2H	formic acid	(methanoic acid)
CH_3CO_2H	acetic acid	(ethanoic acid)
$CH_3CH_2CO_2H$	propionic acid	(propanoic acid)

Esters of carboxylic acids: the suffix -oate is appended in place of -oic or -ic.

$$O$$
$$||$$
$$CH_3CH_2COCH_3$$
methyl propanoate
(methyl propionate)
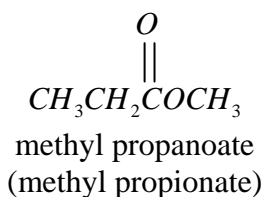
Considerable use is made of Greek letters, α, β, and γ to designate successive positions along a hydrocarbon chain. The carbon attached to the principal functional group is denoted as α, the second as β, etc.

Alkyl Halides

Substituting a halide group for a hydrogen can change the physical properties of an aliphatic compound. For example, although CH_4 is a gas, CH_3I (methyl iodide) is a liquid at room temperature. As the different halides have different properties (e.g.,

electronegativities, size to charge ratios), they will have varying effects. Methyl iodide, for instance, is the only monohalomethane that is not a gas at room temperature. CH_3CH_2Br (ethyl bromide) is the first monobromoalkane to be a liquid. $CH_3CH_2CH_2Cl$ and $CH_3CHClCH_3$ are the first monochloroalkanes in the series to be liquid.

Most haloalkanes (with the exception of fluoroalkanes) have boiling points similar to the alkanes of similar molecular weight.

All alkylhalides have extremely low water solubilities. All iodo-, bromo- and polychloro- substituted alkanes are denser than water.

Alkenyl halides can be more inert than alkyl halides. Vinyl halides are particularly inert. Phenyl and ethynyl halides are also generally inert.

Polyhalogen Compounds

Substitution of additional halogens to a hydrocarbon changes the reactivity of the compound. For example, polychlorination of methane gives:

CH_2Cl_2	$CHCl_3$	CCl_4
dichloro methane (methylene chloride) bp 40°C	trichloro methane (chloroform) bp 61°C	tetrachloro methane methane (carbon tetrachloride) bp 77°C

These are excellent solvents for non-polar and slightly polar substances (e.g. alkanes (oils), etc.). Carbon tetrachloride is used as a cleaning agent. Although the physical properties change monotonically with increasing substitution, for instance, the boiling point rises, the chemical reactivity does not follow the same trend. Methylene chloride and carbon tetrachloride are relatively inert. Chloroform is more reactive.

Fluorinated Alkanes

Some fluorinated alkanes are noted for their inertness. They are commonly used for coolants and propellants. In particular, fluorotrichloromethanes, or as they are more commonly known, freons are used. Examples of flourinated alkanes are:

$CFCl_3$	CF_2CL_2
fluorotrichloromethane	difluorodichloromethane (freon 12)

Freon 12 is characterstic of the difluoromethylene group (that is, if the fluorines are not located on an unsaturated carbon) in that it is fairly inert. The addition of a fluorine to a carbon containing one or more chlorines reduces the reactivity of the chlorines toward almost all types of reagents.

Alcohols

Replacement of a hydrogen with a hydroxide group often dramatically changes physical properties of a hydrocarbon. Alcohols tend to be substantially less volatile and tend to have higher melting points and greater water solubility than the corresponding hydrocarbons. These differences, however, become less as the molecular weight increases. Alcohols can have more than one hydroxyl group and these are known as polyhydroxy alcohols. The simplest of these is methylene glycol:

$$HO - CH_2 - OH$$

Ethylene glycol is miscible with water in all proportions and is used as an antrifreeze.

Aldehydes and Ketones

These groups are distinguished by having a carbonyl group, $-\overset{\overset{O}{\|}}{C}-$

Aldehydes have the general formula $R - \overset{\overset{O}{\|}}{C} - H$ and ketones $R^1 - \overset{\overset{O}{\|}}{C} - R^2$.

The carbon-oxygen bond is both a strong and reactive bond. Formaldehyde adds water reversibly and rapidly at room temperatures:

$$CH_2 = O + H_2O \leftrightarrow \underset{\overset{|}{OH} \quad \overset{|}{H}}{CH_2 - O}$$
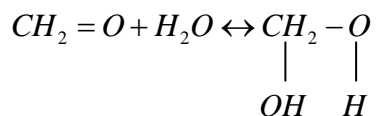
The reactivity of the carbonyl bond is primarily due to the greater elecronegativity of oxygen than carbon. In many aldehydes there is a dipolar resonance. The polarity of the bond facilitates the addition of water and other polar reagents (e.g., *H-X*). However, although the addition is rapid, the equilibrium constants tend to be small (because the strong carbonyl bond).

The effect of the polarity of the carbonyl group is manifested in other physical properties. Aldehydes and ketones tend to have higher boiling points (50 to 80°C higher) than hydrocarbons of comparable molecular weight. The water solubility of the lower-molecular weight ketones and aldehydes tends to be higher than for comparable hydrocarbons. As might be expected, higher aldehydes and ketones are insoluble in water.

Common ketones found in industrial applications (solvents) are acetone $\left(CH_3 - \underset{\overset{\|}{O}}{C} - CH_3 \right)$ and methyl ethyl ketone (2-butanone, $CH_3 - \underset{\overset{\|}{O}}{C} - CH_2 - CH_3$).

Carboxylic Acids

The carboxylic acid group is a combination of a carbonyl group and a hydroxyl group:

$$-C\underset{\displaystyle OH}{\overset{\displaystyle O}{\diagup\!\!\!\diagdown}}$$
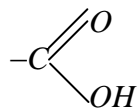
The two groups are arranged so close to each other, that neither group acts independently of the other.

The carboxylic group is considered acidic, because it can donate a proton to a suitable base.

$$RCO_2H + H_2O \leftrightarrow RCO_2^- + H_3O^+$$
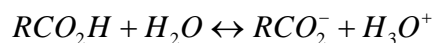
Carboxylic acids can have two acid groups, these are known as dicarboxylic acids. If less than five carbon atoms separate the two carboxylic acid groups, the interactions of the two groups affect the behavior of the acid. One effect is to enhance the acidity of the proton donating tendency, or acidity, of the acid. Common dicarboxylic acids are oxalic (ethanedioc, CO_2HCO_2H), malonic (propanedioc, $CO_2HCH_2CO_2H$) and succinic (butanedioc, $CO_2HCH_2CH_2CO_2H$).

The physical properties of carboxylic acids reflect a considerable degree of association with hydrogen bonding (see Table 8.6). Acids form stronger hydrogen bonds than alcohols, as their $O-H$ bonds are more strongly polarized. In addition, the $O-H$ group on carboxylic acids can form a hydrogen bond to the negative end of the carboxyl dipole.

$$C\underset{\displaystyle O\text{——}H\cdots\ O}{\overset{\displaystyle O\ \cdots\ H\text{——}O}{}}C$$
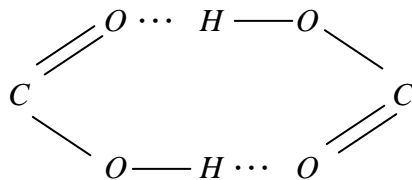
Hydrogen bonding is also responsible for the high water solubility of the simple aliphatic acids. As the alkyl chain increases in length (and in degree on branching) the solubility the aliphatic acid decreases. Salts of carboxylic acids remain moderately soluble in water even when the alkyl group becomes large. Some of the physical properties of carboxylic acids are listed in Table 8.6.

Some common examples of salts of long-chain carboxylic acids are soaps. Acetic acid (or vinegar, CH_3CO_2H) is a common low-molecular weight aliphatic acid.

Table 8.6 Physical Properties of Carboxylic Acids

| acid	structure	solubility g/100 g H_2O	mp, °C	bp, °C	$K_{HA}(H_2O)$ at 25°
formic	HCO_2H	∞	8.4	100.7	1.77×10^{-4}
acetic	CH_3CO_2H	∞	16.6	118.1	1.75×10^{-5}
propanoic	$CH_3CH_2CO_2H$	∞	-22	141.1	1.3×10^{-5}
butanoic	$CH_3CH_2CH_2CO_2H$	∞	-8	163.5	1.5×10^{-5}
2-methylpropanoic	$(CH_3)_2CHCO_2H$	20	-47	154.5	1.4×10^{-5}
pentanoic	$CH_3(CH_2)_3CO_2H$	3.3	-34.5	187	1.6×10^{-5}
palmitic	$CH_3(CH_2)_{14}CO_2H$		64	390	
stearic	$CH_3(CH_2)_{16}CO_2H$		69.4	360 d	
chloroacetic	$ClCH_2CO_2H$		63	189	1.4×10^{-3}
dichloroacetic	Cl_2CHCO_2H	8.63	5	194	5×10^{-2}
trichloroacetic	Cl_3CCO_2H	120	58	195.5	3×10^{-1}
trifluoroacetic	F_3CCO_2H	∞	-15	72.4	strong[a]
2-chlorobutanoic	$CH_3CH_2CHClCO_2H$			101^{15mm}	1.4×10^{-3}
3-chlorobutanoic	$CH_3CHClCH_2CO_2H$		44	116^{22mm}	8.9×10^{-5}
4-chlorobutanoic	$ClCH_2CH_2CH_2CO_2H$		16	196^{22mm}	3.0×10^{-5}
5-chloropentanoic	$ClCH_2(CH_2)_3CO_2H$		18	130^{11mm}	2×10^{-5}
methoxyacetic	$CH_3OCH_2CO_2H$			203	3.3×10^{-4}
cyanoacetic	$N \equiv CCH_2CO_2H$		66	108^{15mm}	4×10^{-3}
vinylacetic	$CH_2 = CHCH_2CO_2H$		-39	163	3.8×10^{-5}
benzoic	$C_6H_5CO_2H$	0.27	122	249	6.5×10^{-5}
phenylacetic	$C_6H_5CH_2CO_2H$	1.66	76.7	265	5.6×10^{-5}

Roberts, Stewart and Caserio 1971

[a]The term "strong" acid means essentially complete dissociation in dilute aqueous solution; that is, the concentration of the neutral molecule is too low to be measured by any analytical technique now available.

Substituted Arenes

We have already talked about some substituted arenes when we first discussed aromatic hydrocarbons. Many reagents that commonly add to the double bonds of alkenes substitute on the aromatic nucleus (e.g., Cl_2, Br_2, H_2SO_4, $HOCl$, HOB_1). The chemical behavior of the substituted aromatic depends on whether the substituted group is attached to a carbon of the aromatic ring and the characteristics of the substituted group.

Aryl halides (with the halide on a carbon of the aromatic ring) are generally less reactive than alkyl or alkyl halides. They generally resemble vinyl halides as they both have their halogen atoms attached to an unsaturated carbon and tend to be nonreactive. Benzyl halides (with the halogen on the alkyl group), are much more reactive.

Br
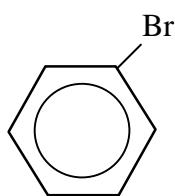
bromobenzene
(phenyl bromide)

CH_2Br
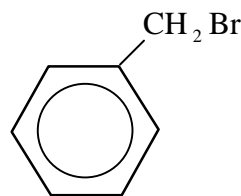
Benzyl bromide

Physical Properties

Aryl halides are slightly polar, and, accordingly, have boiling points approximately those of hydrocarbons of the same molecular weight; their solubility in water is low; their solubility in non-polar organic solvents is high. In general they are colorless, oily, have characteristic odors. With the substituted halogen, their densities are greater than water.

One use of aromatic halides has been as pesticides. The term pesticides includes insecticides, herbicides and fungicides. A number of the most important pesticides are chlorinated hydrocarbons or their derivatives, however, problems with their tendency to accumulate in nature has reduced their use in United States in recent years.
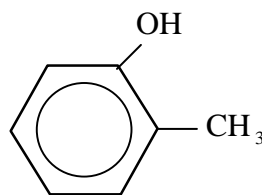
Aryl Oxygen Compounds (Phenols)

Considerable amounts of phenols and cresols ($o-$, $m-$, and $p-$ methylphenols) can be isolated from coal tar (which is formed in the destructive distillation of coal).

Phenols have a hydroxide group attached to the aromatic ring.

OH

phenol

OH

CH_3
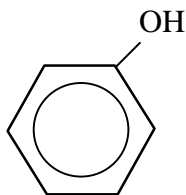
o-cresol

Phenols are more polar, and able to form stronger hydrogen bonds than the corresponding saturated alcohols. This can be seen in the generally higher boiling point, melting point, increased water solubility and acidity.   Phenols are, however, weaker acids than carboxylic acids (by a factor of 10^5).

Heterocyclic Compounds

Heterocyclic organic compounds have cyclic structures in which one or more of the ring atoms are elements other than carbon. Common heterocyclic compounds include nitrogen, sulfur and oxygen compounds.

Four important unsaturated heterocyclic compounds are pyrrole, furan, thiophene and pyridine.   The prefixes az-, ox- and thi- refer to nitrogen, oxygen and sulfur heterocycles. These five-membered rings all possess some degree of aromatic behavior.
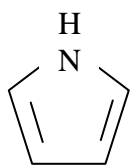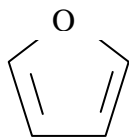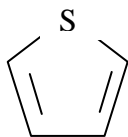
| Pyrrole | furan | thiophene | pyridine |

Three tables follow (Table 8.7, 8.8 and 8.9) that summarize names for compound classes, substituent groups and commonly used abbreviations, respectively.

Table 8.7: IUPAC Nomenclature Summary of Suffixes and Prefixes

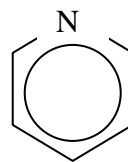| Class	Formula	Suffix	Prefix
Carboxylic acids	$R-\overset{\displaystyle O}{\overset{\|}{C}}OH$	-oic acid	carboxy-
Carboxylic acid anhydrides	$R-\overset{\displaystyle O}{\overset{\|}{C}}O\overset{\displaystyle O}{\overset{\|}{C}}-R$	-oic anhydride	
Carboxylic acid esters	$R-\overset{\displaystyle O}{\overset{\|}{C}}O-R$	alkyl -oate	alkoxycarbonyl- (or carbalkoxy-)
Acyl halides	$R-\overset{\displaystyle O}{\overset{\|}{C}}X$	-oyl halide	haloalkanoyl-
Amides	$R-\overset{\displaystyle O}{\overset{\|}{C}}NH_2$	-amide	carbamoyl-
Nitriles	$R-C\equiv N$	-nitrile (or –onitrile)	cyano-
Aldehydes	$R-\overset{\displaystyle O}{\overset{\|}{C}}H$	-al	alkanoyl-
Ketones	$R-\overset{\displaystyle O}{\overset{\|}{C}}-R$	-one	-oxo-
Alcohols	$R-COH$	-ol	hydroxy-
Mercaptans	$R-CSH$	-thiol	mercapto-
Amines	R_1H_2N $R_2H\ N$ R_3N	-amine *(pri-)* *(sec-)* *(tert-)*	amino-
Ethers	$R-O-R$	- (ether)	-oxa- (or alkoxy-)
Sulfides	$R-S-R$	- (sulfide)	-alkythio-
Alkenes	$R-C=C-R$	-ene[*]	alkenyl-
Alkynes	$R-C\equiv C-R$	-yne[*]	alkynyl-
Halides	$R-X$	-	halo-
Nitro	$R-NO_2$	-	nitro-
Alkanes	$R-C-C-R$	-ane[*]	alkyl

[*]These are suffixes to a root word. The names of alkanes, alkenes, and alkynes are the parent names from which other names are derived by addition of suffixes and prefixes.

Table 8.8: Some Common Abbreviations

Abbreviation	Represents
R-	Any alkyl group
Ar-	Any aryl (aromatic) group
X-	Any halogen atom
Ph-, $\phi-$	A benzene substituent (C_6H_5-)
Me-	A methyl group (CH_3-)
Et-	An ethyl group (CH_3CH_2-)
Pr-	A propyl group $(CH_3CH_2CH_2-)$
Bu-	A butyl group $(CH_3CH_2CH_2CH_2-)$
iPr-	An isopropyl group $\left[(CH_3)_2 CH-\right]$
pri-	Primary
sec-	Secondary
tert-	Tertiary

Table 8.9 Names of Environmental Organic Chemicals*

R–OH	hydroxy group	(alcohol, phenol (R = benzene))
R–SH	mercapto group	(thiol, mercaptan)
R_1–O–R_2	ether	
R_1–S–R_2	Sulfide	(thioether)

$$R_1-N\begin{smallmatrix} \nearrow R_2 \\ \searrow R_3 \end{smallmatrix}$$ amino group (primary amine (R_2 = R_3 = H),
secondary amine (R_3 = H),
tertiary amine, aniline if R_1 = benzene)

$$R_1\overset{\displaystyle O}{\overset{||}{-C}}-R_2$$ carbonyl group (ketone, aldehyde (R_2 = H))

$$R\overset{\displaystyle O}{\overset{||}{-C}}-OH$$ carboxy group (carboxylic acid)

$$R_1\overset{\displaystyle O}{\overset{||}{-C}}-O-R_2$$ ester (carboxylic acid ester)

$$R\overset{\displaystyle O}{\overset{||}{-C}}-S-H$$ thioester (carboxylic acid thioester)

$$R_1\overset{\displaystyle O}{\overset{||}{-C}}-N\begin{smallmatrix} \nearrow R_2 \\ \searrow R_3 \end{smallmatrix}$$ amide

R–C≡N	cyano group	(nitrile)

$$R-N\begin{smallmatrix} \oplus \nearrow O \\ \searrow O \end{smallmatrix}$$ nitro group

R–N=O	nitroso group	

*from Schwarzenbach et al. 1992

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