Chapter 12 – Unsaturated Hydrocarbons

12.1 Occurrence

Although there are quite a number of ways of generating sites of unsaturation in organic molecules there are only two for hydrocarbons the double bond (C=C) and triple bond (C≡C). Hydrocarbon molecules containing one or more C=C bonds are called alkenes. Those with one or more C≡C bonds are called alkynes. One other type of unsaturated hydrocarbon exists: aromatic molecules. Recall these are molecules containing one or more benzene rings. Aromatic systems will be discussed separately at the end of the chapter.

Alkenes and alkynes have very similar physical properties to their analogous alkanes. Alkenes and alkynes frequently have similar reactivity patterns to each other, but differ considerably from the reactivity of alkanes.

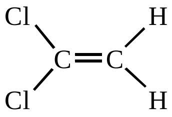
12.2 Naming the Alkenes

Fortunately, the rules for naming alkenes are very similar to the ones for naming alkanes.

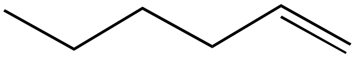
1) All alkenes end in “–ene.”
2) Pick out the longest continuous chain of carbon atoms in the molecule that includes the double bond. Begin numbering from the end closest to the double bond. (Numbering is necessary only if there is some ambiguity about the location of the double bond.)
3) Include substituents exactly as for alkanes except using the numbering scheme developed in (2).
4) For cycloalkenes, do as above except that when numbering chose the scheme that results in substituents having the smallest possible location numbers. Also you must make sure that the carbons in the double bond carry numbers 1 and 2.

As for all nomenclature rules, it may be easier to understand them through a set of examples:

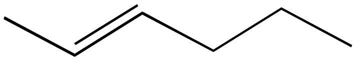
$H_2C{=}CH_2$ ethene (ethylene) No number is need here because there is no ambiguity.



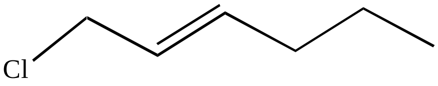
1,1-dichloroethene Here numbers are needed to distinguish between this isomer and one with one chlorine atom on each carbon.



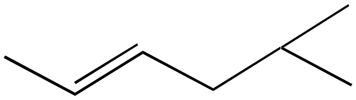
1-hexene



2-hexene



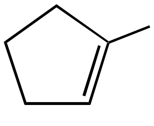
1-chloro-2-hexene



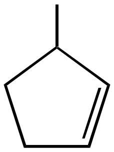
5-methyl-2-hexene

In these examples, the location of the double bond must be explicitly given because there are three potential locations for a double bond in a six-member carbon chain. In each case an incorrect name that looks viable can be developed. For example, you counted from the wrong end the first molecule would be 5-hexene. This is incorrect. Be careful when choosing the longest chain and when numbering it.

You have to be a little more careful when naming cycloalkenes. If a substituent is attached to either of the doubly bound carbons, that carbon is numbered 1. Otherwise, you use the shortest path argument given above.

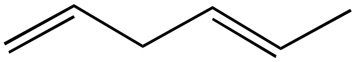


1-methylcyclopentene

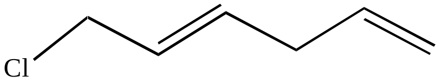


3-methylcyclopentene

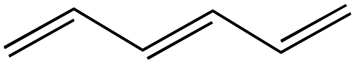
If there are multiple double bonds in the molecule, then they are numbered as described above, except that only the first carbon of the double bond is numbered and a prefix is used to indicate how many double bonds are in the molecule.



1,4-hexadiene



6-chloro-1,4-hexadiene



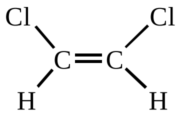
1,3,5-hexatriene

There is one final thing not mentioned in your book that we should touch on. Molecules containing triple bonds are called alkynes. Their naming system is identical to that for alkenes except that instead of the “-ene” suffix, use a “-yne” suffix.

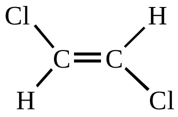
12.3 Geometric Isomers

Just like alkanes, alkenes can also have constitutional isomers (1- and 2-hexene are examples, as are 1- and 3-methylcyclopentene). Recall that constitutional isomers require different atom connectivity (p. 6, Chap. 11 notes). Some alkenes are also subject to geometrical isomerism. Geometric isomers have the same groups bound to each other with same bonds, but differ in the spatial arrangement of the bonds.

Consider 1,2-dichloroethene (this is a constitutional isomer of 1,1-dichloroethene seen earlier on p. 2). Clearly, the chlorine atoms are attached to different carbons, but they may adopt two orientations relative to each other.

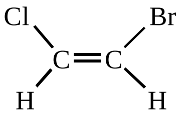


cis-1,2-dichloroethene

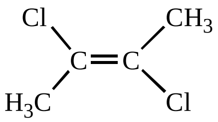


trans-1,2-dichloroethene

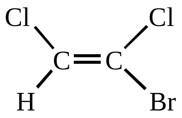
The term *cis* comes from a Latin word and means “on this side,” while *trans* means “across.” These prefixes may even be used when there are two non-identical substituents, or when the meaning is clear. For example:



cis-1-bromo-2-chloroethene

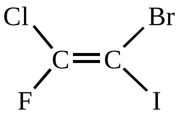


trans-2,3-dichloro-2-butene



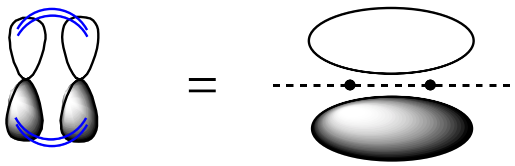
cis-1,2-dichloro-1-bromoethene

Cis and *trans* could not be used for



because the four substituents are all different. One example of geometrical isomers that you may already be familiar with regards a type of fat called “trans” fat. The shape of this atomic arrangement causes some of the health consequences of this fat. We’ll revisit this particular example in Chapter 19.

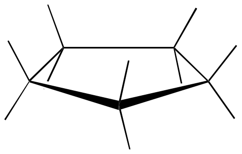
Geometric isomers exist because the C=C bond is rigid and rotation about it is not possible. This has to do with the construction of a double bond. On p. 88 of your book, you saw how two *p* orbitals pointing at one another formed a bond. When this happens the orbitals can rotate without breaking contact with one another, which is why rotation is possible around a single bond. (Bonds like this also happen between 2 *s* orbitals and between *s* and *p* orbitals.) This type of bond is called a σ-bond (sigma bond). A double bond is composed of a single bond of this type and a new type of orbital overlap. Here two *p* orbitals overlap as shown below:



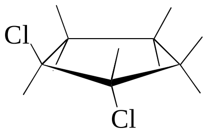
As you can see, if one of the orbitals began to rotate it would break contact with the other (at 90° the break would be complete). Thus, rotation around a double bond isn't possible because it would require the bond to break. This type of bond is called a π-bond (pi bond).

The names σ- and π-bond derive from the fact that the simplest σ-bond comes from the overlap of 2 *s* orbitals, while the simplest π-bond comes from the overlap of 2 *p* orbitals. Single bonds are always made up of a single σ-bond. Double bonds have both one σ- and one π-bond. Triple bonds consist of a σ- and two π-bonds.

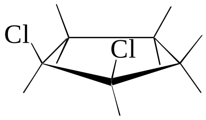
There is one case where *cis*/*trans* isomerism is possible for alkanes. Ring systems also do not have free rotation. Let's look at a cyclopentane ring:



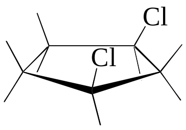
As you can see substituents placed on the same side of the ring could never rotate so as to be located on opposite sides. A result of this is the possibility of *cis*/*trans* isomers. An important difference between alkene *cis*/*trans* isomers and those for cycloalkanes is that for the latter the substituents do not have to reside on adjacent carbons.



trans-1,2-dichlorocyclopentane



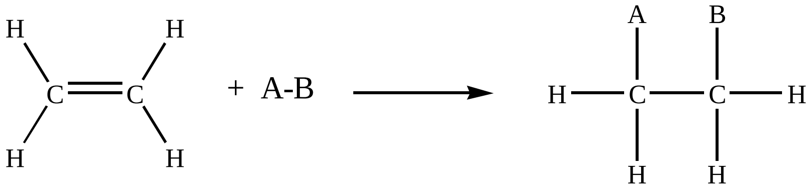
cis-1,2-dichlorocyclopentane



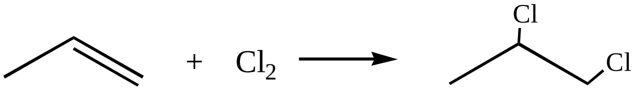
cis-1,3-dichlorocyclopentane

12.4 Addition Reactions of the Double Bond

Consider some alkene and a second molecule A_2 or A-B (e.g. H_2 or HCl). An addition reaction occurs when the A-B bond breaks and A adds to one end of the double bond and B adds to the other end. When this happens the double bond becomes a single bond. Shown pictorially:

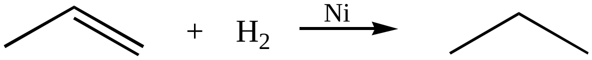


For some molecules this happens quite readily. For example, simply adding either molecular chlorine (Cl_2) or bromine (Br_2) to an alkene results in the rapid addition to form the dihalogenated product.



propene 1,2-dichloropropane

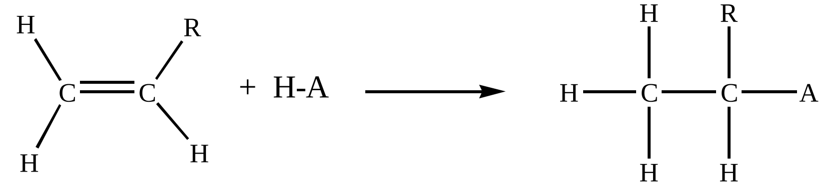
Likewise HCl, HBr, and H_2SO_4 (H-HSO_4) add rapidly across double bonds. In contrast, the addition of hydrogen (hydrogenation) to a double bond usually requires a catalyst. Nickel is usually chosen because it is both effective and inexpensive.

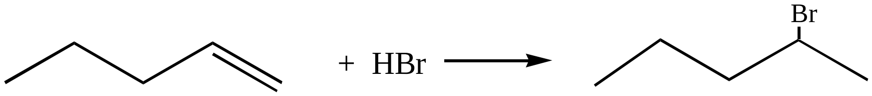


propene propane

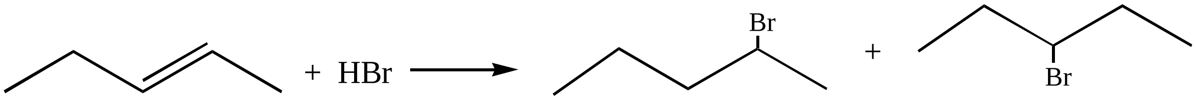
The products of addition reactions are relatively simple to predict when the alkene is symmetrical (the same number of hydrogens are attached to both ends of the double bond) or when the addition product is of the A_2 type. But for A-B molecules adding to unsymmetrical double bonds some care is required. Consider the examples just given. Since in the last example we are adding two hydrogen atoms across the double bond it doesn't matter which goes where because the result is the same. This is also true for Cl_2. But what about H-Cl? The reaction could place the Cl in either the 1 or 2 position. Is either preferred or is it a 50/50 mix?

We use Markovnikov's rule as a guide in these situations. This empirical rule based on many observations tells us that when adding a reagent of the type H-A to an unsymmetrical alkene, the hydrogen always binds to the carbon that starts off with more hydrogen atoms.





You will not encounter any exceptions to this rule in this class. When an addition reagent reacts with an internal double bond and equal numbers of hydrogen atoms are bound to each carbon, a mixture containing each product is obtained. For example, let's look at the last example and, instead of using 1-pentene, let's use 2-pentene.



Water adds across double bonds just like the other unsymmetrical addition reagents, but unlike the others it may require forcing conditions (e.g. heat, pressure). To make an alcohol by addition of water to an alkene, the reaction requires a catalyst (usually an acid) and in many cases significant heat.

$$H_2C{=}CH_2 + H_2O \xrightarrow[240\ ^{\circ}C]{H^+} CH_3CH_2OH$$

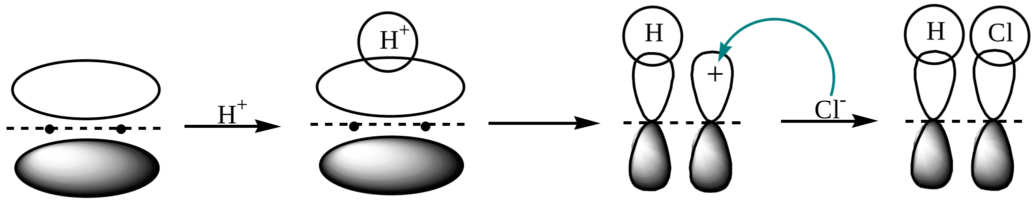
The book also notes that alkenes are susceptible to oxidation by a number of reagents including hot potassium permanganate solutions and ozone. Long term exposure to atmospheric oxygen can, in many cases, lead to oxidation of alkenes. This is why (as was noted in the previous chapter) unsaturated fats have shorter shelf lives than do saturated fats. Light frequently accelerates this process, which is one reason why colored clothing left out in the sunlight fades more rapidly than the same clothing kept indoors.

12.5 How Addition Reactions Occur

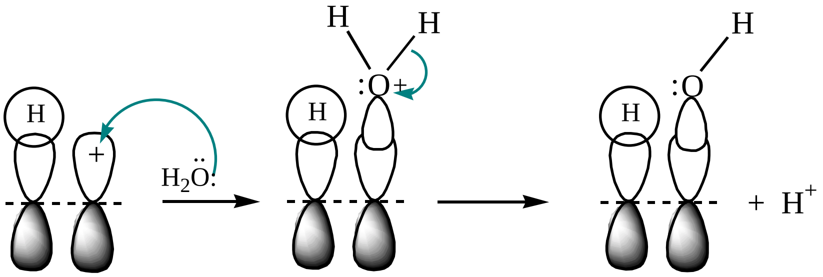
Although most of the addition reactions just presented occur basically the same way, it is easiest to discuss those that involve the addition of an acidic reagent. We'll use HCl as our reagent of choice. Back on pp. 4-5 you saw how the second bond of a double bond comes into being. In this bond a pair of electrons lies outside of the internuclear axis and is more accessible for reaction. The sequence of steps is roughly this:

1) A proton (acid, hydrogen ion) attacks the extended electrons of the double bond (a base).
2) The bond breaks yielding a new C-H bond and a cation on an adjacent carbon (called a carbocation).
3) The anion (in this case Cl^-) combines with the cation.

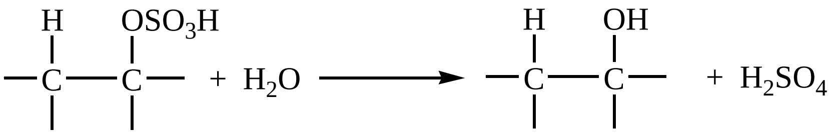
This is can be seen pictorially as:



We can now address why water requires an acid catalyst for reaction to occur. Water is a very weak acid (recall from Chapter 9.4, p. 257), far too weak for the tiny number of protons generated by its ionization to effect the first step. So a proton from the added acid gets the reaction started just like for HCl, except after the first step instead of its anion attacking the lone pair of electrons on the oxygen a water molecule attacks the carbocation. Positive charges on oxygen are unstable, so the electrons in one of the O-H bonds are drawn to it, and a hydrogen ion is released. Here you can see why the added acid is a catalyst. The first step requires the input of an external hydrogen ion and the last step regenerates it.



A question you might have here is "Why doesn't the anion from the acid attack the carbocation instead of water?" After all, the acid suggested by the book in its reactions (p. 376) is sulfuric acid and earlier the book told you that you could add H_2SO_4 across a double bond. The answer is that generally catalysts are added in amounts far smaller than either reagent. Thus while some of the addition product is generated, most of the addition product comes from the primary reagents. The choice of acid can ensure complete generation of the desired product. If you notice, the book always chooses H_2SO_4 as the acid, never HCl. The reason for this is the C-OSO_3H bond is very weak and very reactive. Water easily reacts with it to yield the alcohol product and regenerates the sulfuric acid catalyst. These two considerations assure complete conversion of the alkene to alcohol. We don't use HCl because the C-Cl bond is strong and non-reactive and would result in a mixture of products.



$$-\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{OSO_3H}{\underset{|}{\overset{|}{C}}}- + H_2O \longrightarrow -\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{OH}{\underset{|}{\overset{|}{C}}}- + H_2SO_4$$

The final question we need to address is “So why only Markovnikov additions?” When you look at the reaction scheme either in these notes or in the book, the part that may look strangest is the proton attacking the double bond and yielding the carbocation. Until these past few pages you never saw a C=C bond as a base and electronegativity (p. 109) suggests that carbon is a poor place to locate a positive charge. It is the nature of the generated carbocation that gives rise to the selectivity in Markovnikov’s rule.

Alkyl groups (R) are more electron rich than hydrogen atoms. Consider a carbon atom with three alkyl and/or hydrogen substituent groups; there are 4 possible combinations (CH_3, CH_2R, CHR_2, CR_3). Because they are more electron rich, alkyl groups are better able (than hydrogen) to release some of their electron clouds to the carbon to which they are attached. Thus additional alkyl groups stabilize the positive charge that develops on a carbon when its double bond reacts with a hydrogen ion. The order of stability of carbocations is:

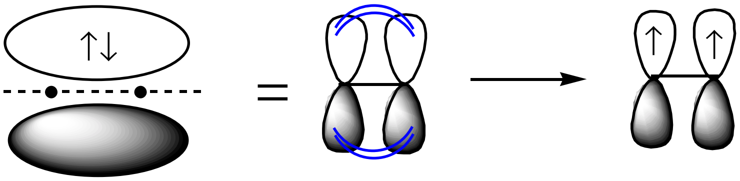
$$CH_3^+ < CH_2R^+ < CHR_2^+ < CR_3^+$$

As you can see on the figure on p. 8 of the notes, after the proton attaches to the double bond it has two carbons to which it can bind. It moves to the one with the most hydrogen ions so that the positive charge resides on the carbon that is better able to accommodate it.

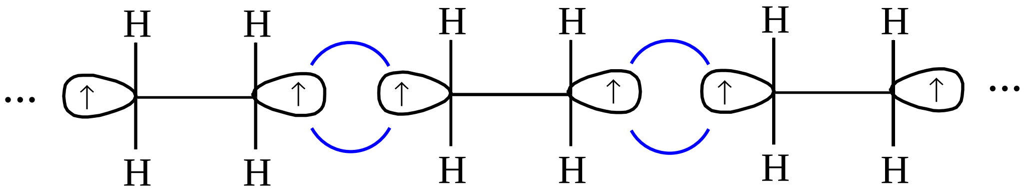
12.6 Addition Polymers

Polymers are important in many facets of your lives. Polymers are commonly encountered as plastics, but many biologically important molecules are polymers as well. Your book begins with a discussion of biological polymers, but I’ll defer those until we reach the appropriate chapters. A polymer is a collection of macromolecules all consisting of the same repeating structural units (Greek = many units). A macromolecule is a very large molecule consisting of a series of structural units that occur many times within a molecule. In polymers there is almost always a repeating pattern, whereas in biological macromolecules there may or may not be a repeating pattern. In a polymer not all macromolecules are exactly the same length (except in unusual cases), while in biological macromolecules lengths may be fixed (e.g. proteins) or not (e.g. certain carbohydrates).

What do we mean by “repeating structural units?” Let’s begin by examining ethylene, $H_2C=CH_2$. Central to the molecule is the presence of two bonds between the carbon atoms, but consider what would happen if that bond were broken such that each carbon had a single electron in a *p* orbital.



Under normal circumstances these orbitals overlap and the electrons associate in the resulting orbital to form a π-bond. If, on the other hand, we reorganize the atom such that the electrons are in orbitals that point at orbitals on other molecules, we can form σ-bonds.



This is the same as -CH_2-CH_2-CH_2-CH_2-. Thus our repeating unit is CH_2. The molecule is called polyethylene because it is made of many (Greek = poly) ethylene molecules strung together. As you might guess, the reaction doesn’t occur as I’ve described in the past few lines. The point here is that when the C-C π-bond in a molecule is broken under the right conditions, we can use the electrons to form new C-C σ-bonds between each molecule and <u>two</u> neighbors.

This offers the possibility of very long chains that we call polymers.

In reality there are a number of different ways of polymerizing molecules. Almost all commercial polymers have a carbon backbone and are formed from the polymerization of alkenes or alkynes. When writing out polymers the repeating unit is usually enclosed in parentheses with a subscript “n” to indicate that there are many of these units present, but the exact number is unknown and varies from molecule to molecule.

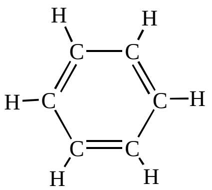
The simplest of the polymers is polyethylene. It has the generic formula CH_3-$(CH_2)_n$-CH_3 where typically n > 10,000 and may be as large as 1,000,000. You know of it as Glad Cling Wrap®. Saran Wrap® is similar:

$$\text{-}(CH_2\text{-}CCl_2\text{-}CH_2\text{-}CHCl\text{-})_n\text{-}$$

If all of the hydrogens in polyethylene are replaced by fluorine atoms one obtains Teflon® and Styrofoam® results from polyethylene where every other carbon is attached to a benzene ring. All of these materials begin with reagents that are qualitatively similar. All are substituted ethenes: Teflon ($F_2C{=}CF_2$), Styrofoam ($H_2C{=}CH(C_6H_5)$). Many other substituted alkenes are polymerized to commercially important plastics. Table 12.2 (p. 387) lists some of them.

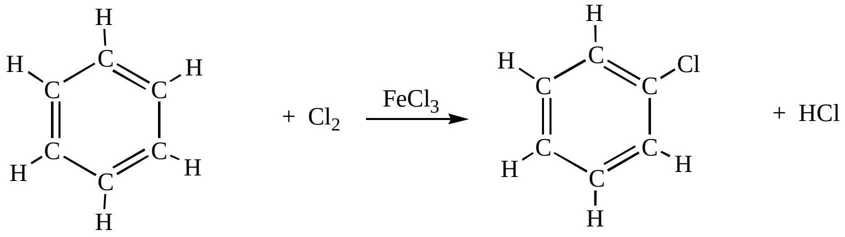
12.7 Benzene Ring and Aromatic Properties

Recall that benzene is a 6 carbon ring with 3 double bonds.

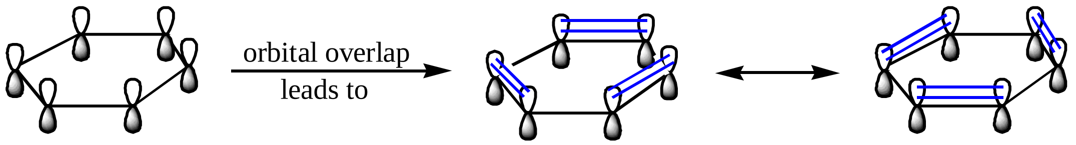


One might expect that this molecule would behave like any other alkene, but this would be incorrect. For example addition of bromine, Br_2, to most alkenes results in the rapid addition of the bromine across the double bond. In contrast, such addition reactions are extraordinarily difficult to accomplish with benzene. In fact, benzene is actually fairly inert to reaction with just about anything.

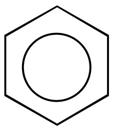
Most reactions of benzene require the addition of heat, a catalyst, and frequently both. The benzene ring is so stable that reaction rarely involves addition to one of the double bonds, rather one or more of the hydrogens is usually replaced. Such replacements are called <u>substitution</u> reactions. A typical aromatic substitution reaction would be:



A question that naturally follows from these observations is "Why is benzene different from a typical alkene?" The (very) short answer is that there is something special about its bonding. You saw earlier in this chapter that part of a double bond results from the side-to-side overlap of 2 *p* orbitals. Now imagine a benzene ring lying on its side. Out of each carbon, perpendicular to the plane of the ring extends a *p* orbital. Each is equally close to both neighboring *p* orbitals. Which does it bond to? Surprisingly, the answer is both, simultaneously. This bond, which



essentially extends around molecule like a ring, is unusually stable and non-reactive. For that reason, instead of drawing individual double bonds, benzene is frequently drawn with only a circle in the center (to represent the ring of electrons).

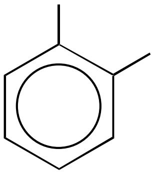


A result of this bonding is that the ring is perfectly symmetrical. That is: all C-C bond distances are the same, as are all C-H distances. All C-C-C and all C-C-H angles are 120º. When benzene rings are attached to other substances they are called phenyl rings.

12.8 Naming Compounds of Benzene

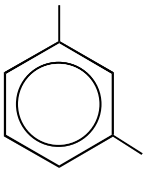
Most compounds of benzene are named by a systematic method. Thus C_6H_5Cl is chlorobenzene, just as you might guess based on naming alkanes and alkenes. A number of benzene compounds have common names and you are responsible for knowing those listed on p. 391.

When there are 2 substituents on benzene there are 3 possible orientations:



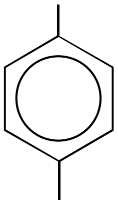
ortho

1,2



meta

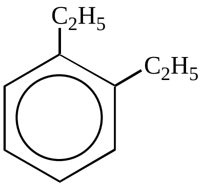
1,3



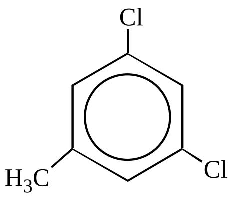
para

1,4

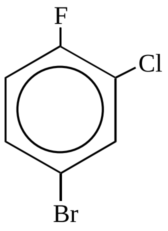
Under the old naming system *ortho*, *meta*, and *para* were used as prefixes. Today the numbering scheme is preferred. It has the advantage of easily allowing for 3 or more substituents.



1,2-diethylbenzene



3,5-dichlorotoluene



4-bromo-2-chloro-1-fluorobenzene