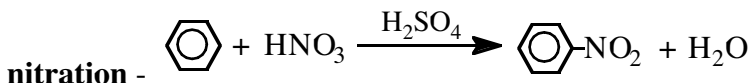
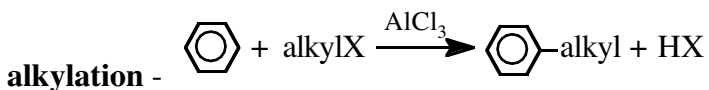
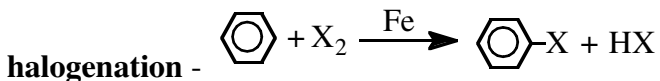
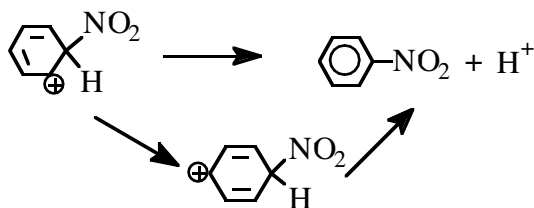
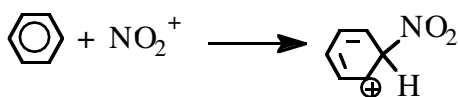


Electrophilic Aromatic Substitution: The aromatic ring is very electron rich, but very stable. The actual reactions that can take place are different than those that take place with ordinary alkanes. Instead of adding molecules across the double bonds, the double bonds are preserved, but the substituents (i.e. hydrogen atoms) are replaced. The common reactions are:



The reactivities of the substituted benzenes are quite varied. Several substituents favor ortho and para substitutions, while some favor meta. The difference depends on the details of the mechanism involved. The mechanism for nitration is believed to be:



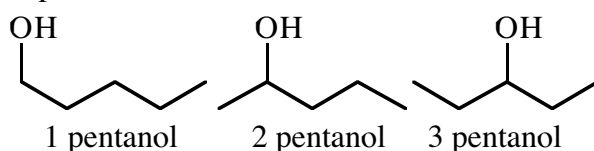
The last step shows that the positive charge on the ring can move via resonance from an ortho to a para position. The presence of a substituent at these positions would prevent certain substitutions from occurring.

Directing Groups: As mentioned before, the position of the electrophilic aromatic substitution depends on the groups bonded to the arene to begin with. Without going into too much detail, the following list describes the positions most likely to be attacked on a substituted benzene ring (i.e. a ring with a side group). It is a handy thing to become familiar with:

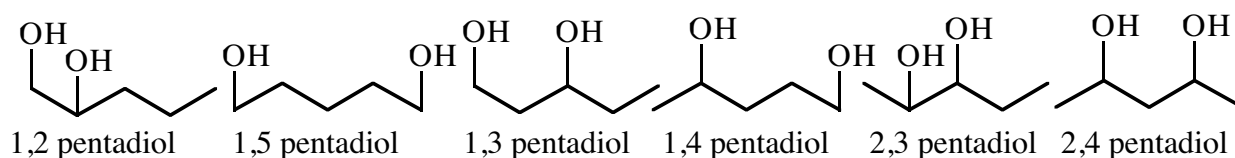
Side Group	Preferred point of substitution
-NH ₂	para, ortho
-OH	para, ortho
-C ₆ H ₅	para, ortho
-OCH ₃	para, ortho
-CH ₃	para, ortho
-NO ₂	meta

-CN	meta
-COOH	meta
-Halogen	para, ortho

Organic Hydroxides = Alcohols: The most fundamental of the oxygen containing functionalities is the -OH group. As a side group, this is called the **hydroxy** group. When it is part of the main chain, it makes the molecule into an **alcohol**. The name of the alcohol depends on the "base name", i.e. the main hydrocarbon underlying the structure. To distinguish between the alcohol and the hydrocarbon, the final "e" in "ane", "ene", or "yne" is dropped, and the suffix "**ol**" is used instead. The position of the OH must, of course, be explicitly stated (in the cases where there is more than one place for the OH to be found). So, for example, we have:



If we have two OH groups on a molecule, instead of "ol" we have a "diol" (for ease of language, the "n" preceding the "ol" is also dropped). This leads to:



Three OHs, triol; many OHs, polyol. A common diol is "propylene glycol" (known to us as 1,2-pentadiol), and it is used in antifreeze.

There are two "rules" you need to be aware of when considering the structure of alcohols. The first is that you NEVER have two hydroxy groups on the same carbon, and the second is you NEVER have an OH bonded to a carbon involved in a C=C (double bond), unless that carbon is part of an aromatic ring.

Physical Properties of Alcohols: The presence of the -OH in alcohols makes these molecules more "water-like", or **hydrophilic**. Hydrocarbons, in general, are notoriously "water-repellent", or **hydrophobic**. The simple addition of an -OH changes everything! Since water is simply H-OH, it is not hard to see why the alcohols are considered to be like water. In fact, some alcohols (namely ethanol - aka "grain alcohol") is so water loving that it prefers being in the presence of water than being pure! This is one of the explanations as to why it is very difficult to get drinking alcohol that is greater than 190 proof (that is 95% ethanol to 5% water).

The larger the alcohol, i.e. the longer the more carbons, the less "watery" it is. Or, another way of saying it is that the bigger molecules are more similar to hydrocarbons. Regardless, all alcohols are comfortable in either setting to a limited extent.

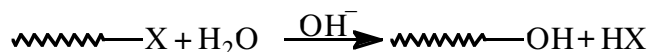
Despite the presence of an -OH, alcohols are all VERY slightly acidic in the Arrhenius sense (though phenols are much more acidic than other alcohols), and they can also act like a base in the Brønsted-Lowery sense (i.e. they can accept H⁺ from a stronger acid, and, as might be expected, phenols are less strong). In fact, many of the reactions of alcohols involve an initial step where the oxygen gets **protonated**, and a subsequent step where H₂O is released (leaving a positive carbon behind).

Formation of Alcohols: In the previous chapter we learned how we could make an alcohol from an alkene. However, this is NOT a really efficient way of making alcohols, mainly because the alkenes are hydrophobic and water (and H⁺) are the other reactants. In any event, there are several other ways of making alcohols that are a bit more useful. Most of them will have to wait a couple of chapters, but four are worthwhile mentioning here.

The first method is the oldest known biochemical process ever exploited or investigated by humans. It is known as **fermentation**, and it is the process by which sugars are converted into alcohols. Depending on the sugar you start with, the alcohol you get can range in size and toxicity. Wood alcohol, aka methanol, is an example of a toxic alcohol that can be produced by fermenting cellulose (a polymer of sugar). This is an industrially and economically very important process. However, it is not what we call “classic” organic chemistry.

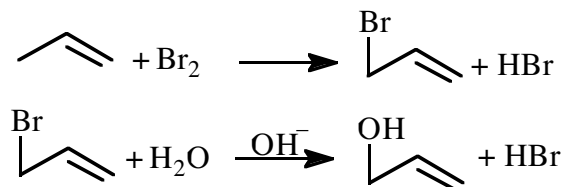
The second, industrially relevant process is not new to us in this course. It involves cracking petroleum products in the presence of steam. In this way, not only are shorter alkanes and alkenes (and alkynes) produced from long chain molecules, but alcohols are also generated. But, as in the alkane/ene/yne cases, you can't be sure what you are going to get before you start, and you never can tell how much you'll get either.

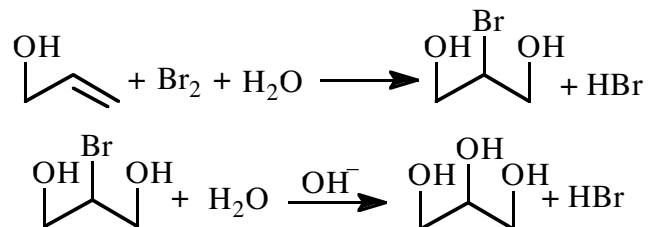
The third one, known as a **nucleophilic substitution**, a halo-alkane is made into an alcohol simply by putting the halo-alkane in the presence of water (and, sometimes, OH⁻, depending on how reactive it is). In this reaction, the halide ion pops off the hydrocarbon and the hydroxide takes its place:



The squiggly line represents a generic hydrocarbon. These reactions are good for making alcohols from simple starting materials, and are especially good for making poly-ols from alkenes.

In the following sequence of steps, we will make propanatriol (aka glycerine or glycerol) from propene:





These are all fairly efficient steps, so we expect pretty good overall yield.

The fourth method is a bit scarier than the previous one, because it involves stuff we have not seen before! But, fear not, we can do it! This reaction is called **hydroboration-oxidation**. In this reaction, an alkene is treated with B_2H_6 (diborane), and then with H_2O_2 (hydrogen peroxide) in the presence of OH^- . This gives the anti-Markovnikov product. Since this is a bit obscure, we will ignore it for now.