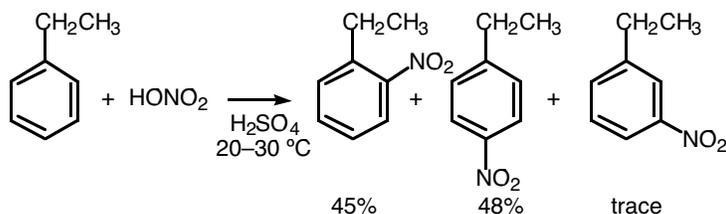


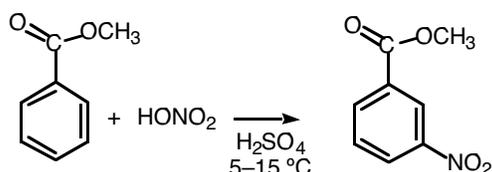
### Some additional notes on aromatic reactions

We discussed that some substituents on benzene rings can have a directing effect on a second substituent. These are split into two groups: ortho,para-directing and meta-directing:

ortho,para-directing



meta-directing



Some of the groups were listed in the previous lecture notes. If we examine these groups we will see some trends. Ortho,para-directing groups tend to have at least one pair on non-bonding electrons directly adjacent to the aromatic ring. These will have the tendency to be able to donate electrons to the aromatic ring. Notable exceptions here are alkyl groups. To contrast, meta-directing groups will tend to withdraw electrons from the ring, even to the extent of having a positive charge next to the ring.

### Resonance

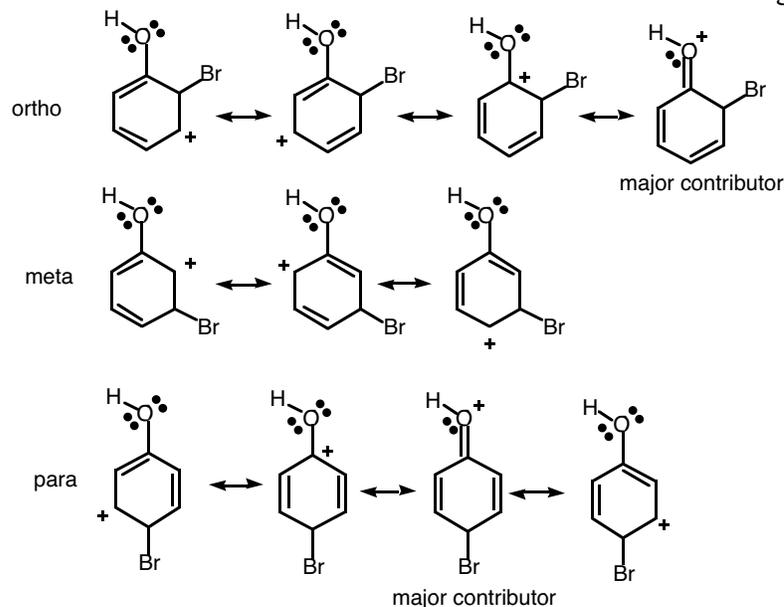
The selectivity of these directing groups can be rationalized through the examination of the resonance structures of the reaction intermediates. For many molecules (intermediates included) we find that they can be represented by several different Lewis structures. This is not to say that the molecule exists in all of these forms separately. In reality the molecule is a hybrid (a combination) of all of the resonance forms (also called resonance contributors). Resonance has helped to explain many experimental results where a single Lewis structure could not.

There are several basic rules that should be followed when considering resonance structures:

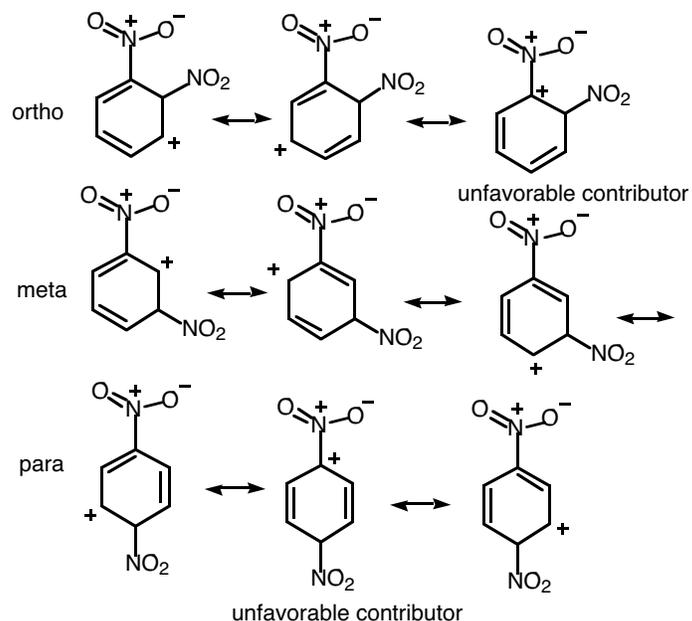
1. Resonance contributors have the same connectivity. Only nonbonding electrons and electrons in multiple bonds change locations from one resonance contributor to another. The electrons in single bonds are not involved.
2. The nuclei of the atoms in different resonance contributors are in the same positions.
3. All resonance contributors must have the same numbers of paired and unpaired electrons. Thus they will have the same total charge.
4. Resonance contributors in which there is little or no separation of charge are more important than those with a large separation of charge. Ones containing adjacent like charges are highly un-favored.

### Intermediates of Electrophilic Substitution Reactions.

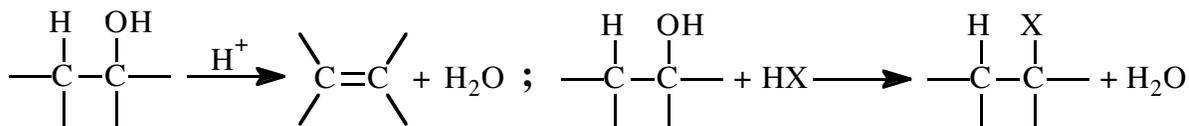
Here is an example of some resonance structures for intermediates of a reaction involving a benzene ring substituted with an ortho,para-directing group. The scheme depicts the possible resonance structures of an intermediate when the electrophile (bromine in this case) attached to all the possible unique positions on the benzene ring. Important to see is that the ortho and para intermediates are more stable. The presence of the alcohol draws charge away from the aromatic ring. These are the resonance contributors that have 8 electrons around each of the atoms on the benzene ring.



Meta-directing groups tend not to have any really stable resonance contributors as seen with ortho,para-directing groups. More precisely they have resonance contributors that are not as destabilized as the others. In general it is usually harder to react aromatic compounds with meta-directing group (compared to ones containing ortho,para-directing groups) since it is more difficult to form the carbocation intermediate. In the scheme below note the resonance contributors that have positive charges on directly adjacent atoms. This is not observed in the meta intermediate set.



**Reactions of Alcohols:** The reactions that alcohols can be involved in are numerous. The simplest reactions, i.e. the reverse of halogen substitution and the opposite of the hydration of a double bond:



Notice how both of them require the presence of  $\text{H}^+$ , because both reactions involve the protonation of the  $-\text{OH}$ , and the subsequent release of water.

But, there are other reactions that are very important that involve the alcohol behaving like an acid. Since they are very weak acids, the base that deprotonates them must be very strong. Like water, when an alkali metal (Li, Na, K, Rb) is put in contact with an alcohol, the metal gets oxidized, and the acidic proton on the  $-\text{OH}$  gets reduced (to form  $\text{H}_2$  gas):



The anionic product (i.e. the negative ion produced) is called an **alkoxide** ion. The name depends on the specific alkane that corresponds to the main chain. The alkoxide ion is very important in the formation of ethers, which we shall see shortly. Interestingly, the alcohols that react the most readily in this type of reaction are the  $1^\circ$  (then  $2^\circ$ , then  $3^\circ$ ). The reason involves the electronegativity of the oxygen, and will be discussed if there is sufficient interest.

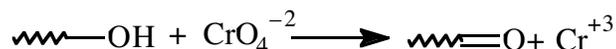
The next reactions are also redox reactions, but the hydrogen is not being reduced. Rather, the carbon bonded to the oxygen is oxidized. These reactions are summarized as follows:



where [O] means the oxidizing agent, and the choice of product depends on the reactants (both the alcohol and oxidizing agent). Note, 3° alcohols do not react in this way.

The last reaction we can mention at this point is the **ester** formation reaction. However, we will wait until the carboxylic acid chapter to fully explore this.

**Oxidation by Chromic Acid:** A very interesting reaction is that of alcohols with chromic acid. Chromic acid is a source of the **chromate** ion,  $\text{CrO}_4^{-2}$ , which has a distinctive yellow/orange color. When the reaction:

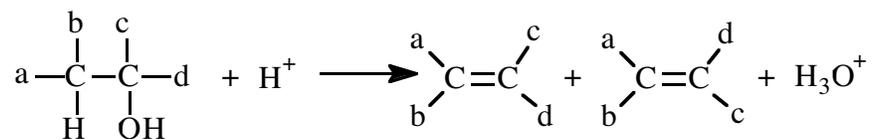


the solution changes color to a kinda yucky green.

The ease of this reaction, and the fact that it does not require a large amount of alcohol to work, made it the "choice" reaction for the original "**breathalyzer**" tests. People suspected of driving drunk were asked by the police to blow up a baggie that contained the chromate ion. The alcohol in their breath would react with the  $\text{CrO}_4^{-2}$ , producing a nasty green color if they were in fact "legally" drunk. The new breathalyzers are electronic, and operate on a completely different principle.

**Dehydration of Alcohols:** As mentioned, another very important substituent on an alkane chain (besides halogens) is the **hydroxyl** group, -OH. Carbon chains that have hydroxyl groups on them are called alcohols. We will talk much more about them later, but, it should be pointed out that they can be used to form alkenes.

In these reactions, an alcohol is reacted with a strong Arrhenius acid (i.e. a source of  $\text{H}^+$ ), and water and the alkene are the products:



The  $\text{H}^+$  is also reformed (illustrated above by  $\text{H}_3\text{O}^+$ ). The reactivity of the alcohol depends on what kind of carbon has the OH on it. The order of reactivity is  $3^\circ > 2^\circ > 1^\circ$ .

It should also be pointed out that this is NOT a way of making alkynes! The diol (i.e. alkane with two hydroxyls) that has two hydroxyls on the same carbon is NOT stable, and an OH bound to a carbon with a double bond to another carbon is also not stable. Therefore, either the starting material for the first elimination, or the product of the first elimination is not stable.