

Lecture 6B • 10/08/11

Let's jump into these functional groups. A little bit of terminology first. You've probably heard about saturated and unsaturated fats. The term saturated means it contains the maximum possible amount of hydrogen. In other words, every carbon has only single bonds to other carbons, or besides carbons, it has single bonds to everything else. So saturated means maximum amount of hydrogen attached possible. Unsaturated, our first definition of it will be, contains double and triple bonds. To be a bit more complete, we'll learn that one way of viewing unsaturation is to have a ring. If we imagine hexane – six carbons – at one end or the other, there's going to be three hydrogens on each of those end carbons because they are primary carbons, carbons attached to only one other carbon. If you took those two carbons and joined them in a circle, though, you'd have to remove one hydrogen from each end so that there was a place to make a new carbon-carbon bond. That's why a ring is sometimes considered a form of unsaturation.

The reason for mentioning this terminology is because I tend to divide functional groups into two broad classes: saturated functional groups, unsaturated functional groups. First, even before that, there are just the hydrocarbons. When you have just carbon-carbon single bonds and that's the only important structural feature of the molecule, that's called an alkane. If you have a carbon-carbon double bond, that makes it an alkene; and if you have a carbon-carbon triple bond, that makes it an alkyne. Those are the only types of functional groups we have with just pure hydrocarbons.

The next group would be the saturated groups – more specifically, the saturated heteroatom groups, which I like to organize the reverse direction from the periodic table, starting from the righthand side of the periodic table, moving to the left. So, first type of functional group that we'll get is alkyl halides. Remember that the -yl ending in the name means a substituent, so what alkyl halide means is you've got some kind of alkyl group attached to the halogen. This X almost always means either fluorine, chlorine, bromine, or iodine. It's a variable name that so commonly used, you need to be familiar with it. Along with that, there is a variable name for carbon groups: R for radical. The word radical means something that sticks out – like radius – sticks out from the center of something. These different substituents are also called radicals. R, for right now, will mean an alkyl group of some sort.

Next column of the periodic table: the chalcogens, which include oxygen and sulfur. The first group is called an alcohol; it has an oxygen connected to just one carbon [and one hydrogen]. If you have a carbon on either side of the oxygen, if you have an oxygen connected to two carbons, it's an ether. The term ether itself can refer to this specific compound diethyl ether, but the word ether is actually a functional group name. If you have two oxygens that are connected to each other, it's called a peroxide [or hydroperoxide if either oxygen has a hydrogen]. The [per] means extra or maximum, so more oxygen is what it really means. Why does this have that different oxidation state? The single bond, because you have two of the same atoms involved, you would have to cut this bond evenly, whether you're determining formal charge or oxidation state. Oxygen, being more electronegative than carbon, would get both of the electrons in a bond with carbon, so you'd end up with seven electrons around oxygen, versus the six you would have as an element on the periodic table, so 7 versus 6 gives you that -1 oxidation state.

Oxygen makes compounds with carbon; so does sulfur. The equivalents of an alcohol, an ether, and a peroxide are known as thiols, sulfides, and disulfides. Thiols are really, really stinky. When you use the gas in the lab here, when it leaks out, you don't actually smell the gas, per se. Natural gas has little, if any, odor to it. Because of that, so that we know if there's a leak or not, they take just tiny, tiny quantities of thiols and add it to the natural gas. If you were to take a drop of ethanethiol and drop it into the classroom, we'd have to evacuate the building because that's how bad it would stink. Sulfur compounds tend to be stinky. That's the chalcogen group, oxygen's column.

Now the pnictogens, nitrogen's group. This is an amine. Because of the reactivity of nitrogen, how it differs from oxygen or carbon, a compound is called an amine whether it has one group on it or two or three or four. These terms primary, secondary, tertiary, quaternary: they're used differently with nitrogen. A primary amine is one carbon on nitrogen. This would be a secondary amine; tertiary amine. Then, if you tried to put one more alkyl group on it, you're gonna end up making a cation. Rules of formal charge: each bond counts for one electron. Cut all the bonds to nitrogen: that gives you four electrons, compared to the five it would have as an element, so that's why it's a plus charge, so that's called a quaternary ammonium ion or salt (with whatever it's paired up with). So same terms – primary, secondary, tertiary, quaternary – but because nitrogen is different, the terms are used differently.

For these other functional groups, the normal terms of primary, secondary, and tertiary apply. For example, this is a secondary alcohol. Why? Because the position of the oxygen it's attached to is a secondary carbon.

Amines, because they give up their lone pairs so easily, amines are actually weak bases. That changes how they react, so that's why we classify them differently. Nitrogen can tolerate a plus charge. Sulfur, oxygen can't; those kinds of compounds are [normally] very unstable. But this, you can easily get an ammonium salt and isolate it, no problem. {phosphorus}

I want to give you a sampling of unsaturated functional groups. The halogens can form multiple bonds, but multiple-bond compounds with carbon rather exotic. For the chalcogens, first with oxygen Notice that on one side, where R notation has been used, we have an alkyl group; on the other side, we have to have a hydrogen. When you have that combination of alkyl group and hydrogen, this is called an aldehyde. If, instead, you have two alkyl groups, no hydrogen, very similar reactivity, some important differences as well, so it's a distinct functional group called a ketone. {Sulfur}

Nitrogen. You could call it the nitrogen equivalent of a ketone, cause it's got a carbon-nitrogen double bond. This is called an imine. So we have amines and imines, and if that's not good enough we'll have, later on, amides, imides, and enamines. We're going to have all of these amine-sounding names.

After this, there's a whole bunch of carboxylic acid derivative functional groups.

The carbon-oxygen double bond itself is called a carbonyl bond.

Let's come back to some nomenclature rules. {review of rules introduced in lecture 5B}

Now let's tackle rules for handling different kinds of substituents. There is something known as functional group priority. You can have a molecule, for example, that has an alcohol, a ketone, and an alkyne, all in one molecule. How do you name it? You have to figure out, between those different functional groups, which one is called the most important. As a general rule, it will be the different carboxylic acid derivatives that have the highest priorities – carboxylic acids, amides, imides, acyl halide, anhydrides. Below that are the unsaturated groups – ketones, aldehydes, and imines. Below that, we have the saturated heteroatom groups. A ketone would be considered more important than an alcohol, for example. Below that, we have the [pure] hydrocarbons. Below that are the halogens. So chlorine, bromine, fluorine, and iodine, never actually get a functional group ending; you don't have a name end for those. They're always just substituents. So, if you have a fluorine, chlorine, bromine, or iodine, they get the prefixes fluoro-, chloro-, bromo-, and iodo-.

Let's name a couple of simple molecules. What if we had two functional groups? Or, let's start with two of the same functional group – two bromines. In the name, for clarity's sake, we put in a prefix to say how many of each group do we have. These are referred to as multiplicative prefixes. They are ones that you might have encountered when naming binary covalent compounds: mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-. I'm putting a star by mono, because we don't generally use the mono prefix, not for simple compounds. The fact that we have two bromines, we'll stick a di- in front of bromo- to show that we have two bromines. If we wanted to number this compound, would I number from the left or the right? The left, because the number 2 would happen if we numbered from the left, the number 5 would happen if we numbered from the right. It is, therefore, the correct way to do from the left. Every substituent, we always name its position. Even if there's two on the same carbon, you name each one of them. This compound, putting this all together, would be 2,3-dibromohexane. Notice we use commas between numbers; between numbers and letters, there are dashes. The parent name always comes at the end, and since halogens are less important than alkanes, that's why we have the -ane ending.

Another example. We've got two functional group. We'll name each of them and join them in a chain in the name. Which one do we name first? Why would you say bromo? For writing the name out, it is done on alphabetization. We're going to name bromo- before chloro-. We have to name bromine's positions; we have to name chlorine's position. Number from the left will give us the lowest starting number. It doesn't matter which functional group gets the lowest number, it's that any functional group gets the lowest possible number [only applies to halogens; needs correcting for general case]. Rule #3: substituents are listed in order of alphabetization. So this compound would be 2-bromo-3-chloropentane.

Even if we swapped the chlorine and the bromine, we would call it 3-bromo-2-chloro[pentane], because, still, numbering from the left, the two would be lower than if you give it a 4, like you said.

Another easy case that gets us into one of the finer rules. Regardless of which way you number this compound, you'd get a 2,4 or a 2,4, so the numbers are identical. How do we figure out which way to name the compound, then? In that case, you'd go in order of alphabetization. So, in this case, we'd give the bromine the number 2 because it is alphabetically lowest. If numbering from multiple directions gives the same locants, priority is given to the group that appears first in alphabetical order. So the correct way of numbering this would be from the right. So this would be 2-bromo-4-chloropentane.

An alcohol is more important than any hydrocarbon or halogen. If you just have an alcohol as the main functional group, it will establish the priority of the molecule. We will number giving the alcohol position the lowest number. Alcohols are also more important than substituents that are just alkyl groups or halogens. Notice that when I numbered this, I did not give a number to the oxygen itself; only carbon, generally, receives numbers when numbering compounds. This is an alcohol. How do I show that? There's the old style and new style. I greatly prefer the new style, but most texts and most chemical bottles are still using the old style. Old style, you'd say 1-butanol. So in any for the alkanes that end in -ane, drop the -ane ending, add -ol, and that's how you make an alcohol name. To more clearly specify what the number means, the new style puts the number right before the functional group, so it'd be butan-1-ol.

Just to show a slightly larger example molecule, and again getting to priorities. A higher-priority functional group takes precedence over lower-priority functional groups for purposes of numbering. If I number from the left, I get 2 and 4; if I number from the right, I get 2 and 4. How do we decide between the two? The alcohol functional group is more important than the alkyl substituent, because hydrocarbons are less important than alcohols. Because of that, we're going to number this from the left. This would be called 4-methylpentan-2-ol, using the new style. To show the old, it would be 4-methyl-2-pentanol.

What if you had multiple alcohols? Just like we show how many of each substituent that we have, we then also show how many of each functional group that we have. This compound would be pentane-1,2-diol. Notice, there is an e in this name, where there's no e up above. That's for purposes of – elision, is it called? If you had butaneol, in English [at least] if you put the e and o together you might be tempted to pronounce it some other way. To make a smoother transition, you drop the e if there's going to be a vowel there anyways. But in the name down here, if you put the n and the d together, to make sure the -ane is pronounced correctly, you stick the e back in. So when you have two consonants that are going to bump, the e stays in; you got a consonant that would be followed by a vowel, you'll leave the e out.

Looks more complicated, but evaluating the molecule from left to right, that is the longest chain. If we look at it, there's 10 carbons, so it's a decane. Would I number from the left or the right? From the left. From the right, my first number is 4; from the left, my first number is 2. Doesn't matter which kind of functional group, how many functional groups or substituents, these are all alkyl substituents – same priorities in terms of functional group priorities. So whichever direction gives me the lowest number, I go with it, so I'll number from the left. What kinds of substituents do I have? I have methyl substituents on the left of the molecule and ethyl substituents in the middle of the molecule. How many methyl substituents do I have? 2 of them, so part of the name is going to be 2,2-dimethyl-. How many ethyl substituents do I have? 3, so we're going to name part of the molecule 5,6,7-triethyl-. Which one do I list first? Why ethyl? Because e comes before m. But what about the dis and tris? You ignore them. You ignore simple prefixes when alphabetizing. The m in methyl is beat out by the e in ethyl. Rule #6: simply multiplicative prefixes are ignored for purposes of alphabetization. So this compound would be named 5,6,7-triethyl-2,2-dimethyldecane.

The iso and neo attached prefixes are alphabetized, but unattached prefixes, such as sec- and tri- are not used, unless you are comparing a sec- and a tert-butyl functional group. But, we don't even use any of those names in purely substitutive nomenclature; that's why I called them common names. In real life, chemists will use a mixture of the two systems.

Let's start talking about alkenes. You'll see very quickly why they are trickier. It's an important point that single bonds rotate but double bonds can't. First, just to name an alkene, if the alkene is the only functional group in the molecule, it takes priority over any alkyl groups or halogens. You give the alkene the lowest possible number. There are always two carbons involved in an alkene, so we name the first one you come to. So, the alkene's closer to the right than the left so we'll number from the right. Since the first carbon of the alkene is 1, the lower number of the alkene is 1, we use it to name it. So, this is pent-1-ene. From now on, I'm only going to use just the new style of nomenclature. If you answer the old style, I wouldn't mark it incorrectly. 1-pentene.

What if we had two alkenes on the same molecule? This would be octa-1,7-diene. Why 7? Because either way we number it, it's going to be equivalent. But 7 is the lower of the numbers that would be associated with the second alkene. What if we had something like 2-pentene? That would be fine as a name, except that's not enough, because – which 2-pentene? Since double bonds cannot rotate internally, configuration of substituents to alkenes are locked in. There are two unique possibilities if you have one substituent on each side.

Sometimes we care what's on the left carbon versus the right carbon, so one side versus the other. But when we start talking about reactions, we'll talk about things reacting with the two positions sticking out this way or the two positions sticking out that way, so one side or the other. But if I then just say the phrase "one side or the other", do I mean left or right, do I mean top or bottom? Here's the way I'm going to tackle it. If you're talking about the left or the right part of the double bond, when you chop this way, then I'll call these the side. If I'm talking about the top and the bottom (when written this way), I'm going to refer to those as the two faces of the double bond.

If you've got one substituent on either side of the double bond, like I've got here, are they on the same face or opposite faces? They're two unique molecules. If you had them pointed in opposite directions, what do we call that kind of configuration? It is trans.; cis would be together. So trans, you can think of as opposite; cis you can think of as the same. These compounds could be named as trans-pent-2-ene or cis-pent-2-ene. The terms cis and trans can only be used when only groups are being compared. We only have one substituent on one side and another substituent on the other side that we're looking at. The relative position of those two, we can use cis or trans. But what about a molecule like this? Is it cis or trans? The answer is yes; it's both. But it can't be both, we can't name it that way, so you can't cis or trans to name this molecule. So, there's two other symbols that we use: E – entgegen; Z – zusammen. Opposite and together. So, E is the equivalent of trans, Z is the equivalent of cis. E and Z can always be used wherever cis and trans can be used [when naming double bonds].

Cis and trans can only be used if you're only comparing two objects. What we have to do is figure out on each side, which is the most important group? To name this alkene, the most important group on each side must be identified.

On the right, we have carbon versus hydrogen. This is the first of what are called the CIP (Cahn-Ingold-Prelog) priority rules, named after the scientists who formulated this naming procedure for dealing with stereoisomers. Rule #1: higher atomic number is given priority. So on the righthand side, we have carbon versus hydrogen, so the carbon group is more important. Rule #2: if you can't figure it out from the first carbon out, you go to the next carbon. If priority cannot be established at the point of attachment, then the next point out is compared. To highlight what is here, I will write my hydrogens in. According to the normal rules, we wouldn't write those hydrogens in, but there's nothing saying I can't do it if I want to highlight the fact that on the left, we have carbon at the point of attachment for both substituents. For comparing carbon and carbon, they're the same, we can't figure out which one wins; so we go the next thing out, whatever's attached. On the top, there's just hydrogen attached; on the bottom, we have a carbon attached. That falls back to rule #1: higher atomic number wins. It happens to be the longer chain that wins in this case, but it's not always true. The name of this compound would be (Z)-2-methylhex-3-ene. The Z is a stereodescriptor. You're seeing the first example of a name that has pretty much everything in it: a stereodescriptor, locants, substituents, parent name, and a functional group ending.

Remaining written notes and structures same as lecture 6A

To name this alkene, the most important group on each side must be identified.