

Lecture 6A • 10/07/11

Functional groups

A bit of terminology before we get to functional groups themselves. Some terms you may have heard in relationship to food before – saturated and unsaturated. Saturated refers to a molecule that has the maximum amount of hydrogen attached possible, based on the number of carbons present – which is going to mean that you end up with all single bonds. Alkanes – those would be considered saturated hydrocarbons, because they only have single bonds. Unsaturated generally refers to the fact that something contains double or triple bonds. The reason why, in terms of food, unsaturated fats are healthier is because they do have these double or triple bond functional group which are much, much, much more reactive than alkanes. It gives the body a place to grab on to metabolize these compounds. To make this a technically more complete definition, I'm going to add this comment: that the term unsaturated sometimes refers to rings.

If you imagine the molecule hexane, either end of hexane is a methyl group, which has three hydrogens. If we turned it into a ring to make cyclohexane, we'd have to take one hydrogen off of each end to form that new carbon-carbon bond. Since we removed hydrogen, that's why sometimes a ring is considered a form of unsaturation.

Let's look at the different flavors of functional groups, starting with the pure hydrocarbon functional groups. There are only three. If you only have carbon-hydrogen [and carbon-carbon] single bonds, then that is an alkane. If you have a carbon-carbon double bond, that is an alkene; and if you have a triple bond, it is an alkyne. Next family of functional groups I call the saturated heteroatom groups. I like to classify these in reverse order of the periodic table, starting from the righthand side of the periodic table and moving left. First group are what could be either called alkyl halides, the common-name form of it, or more properly, haloalkanes. X is a variable name that usually means halogen – fluorine, chlorine, bromine, iodine. If you're using X, you're trying to signal that it doesn't matter which one is there; one of these should be present. There's a variable name that's used for carbon groups – R, which stands for radical. Radical isn't just a compound with a single electron on it; where that term comes from is the fact that if you have something that's core to the molecule and then you have things sticking out, the thing that sticks out is the radical, so the radical is the thing that sticks out. That's how this term for R came about.

The next column with oxygen, those are the chalcogens. R is showing that it doesn't matter what's attached. To make it more explicit, R = H or alkyl, for the following examples. If you have oxygen, there are three main functional groups that we have: an alcohol. If you have carbons on either side of the alcohol If you look here, you see that I specifically have a hydrogen; you have to have a hydrogen on the oxygen to be an alcohol. For an ether, it has a carbon on either side of the oxygen. If you had just two carbons total, so the R was a methyl group If you had two carbons total on either side, that's diethyl ether, which we call just ether out of laziness, but ether is technically a functional group name as well. Then, the last group, where you have two hydrogens that are attached to each other, that's a peroxide. Why does it have its unusual oxidation state? Remember the rules for oxidation state: oxygen is more electronegative than carbon, so, in counting electrons, we would give two electrons to each oxygen from the carbons that are attached. Since oxygen is bonded to itself, that has equal electronegativity since it's the same atom, we fall back to dividing the bond evenly in half. So, each oxygen, if you were to break it up, would have seven electrons, which compared to the six it would have as its place on the periodic table – 6 versus 7 that's how you get the -1 oxidation state. There are the oxygen groups.

There are equivalent sulfur groups. This first one – thiol. The next one is called a sulfide; the one after that – a disulfide. Thiols, just as a side note, are enormously stinky compounds. For example, the natural gas that we have in the labs that we're using, natural gas doesn't particularly have an odor. What they do is they add very, very small portions of a thiol, so that we can smell it in the leaks and we know to do something about the gas leak. If we took a thiol and dropped a drop in the middle of the room here, this entire building would need to be evacuated just because of how powerfully stinky it would be. Human sense of smell is particularly sensitive to sulfur.

These terms primary, secondary, and tertiary apply to the functional groups that I've shown you so far. Since the oxygen of this first example is attached to a secondary carbon, this is a secondary alcohol. Because this thiol is attached to a carbon that has three other carbons on it, this is a tertiary thiol. These terms primary, secondary, and tertiary work for most functional groups, except for the one I'm about to show you.

When we have nitrogen with saturated bonds: this functional group is an amine. Nitrogen has very different reactivity than oxygen or the other heteroatoms, because nitrogen is basic. Amines, like ammonia itself, those lone pairs are able to become protonated, form bonds with hydrogen, so it is a weak base therefore. Because of this difference in reactivity, oxygen never likes to carry a positive charge. We name amines differently, we classify them differently. The terms primary, secondary, and tertiary no longer refer to what kind of carbon that the nitrogen is attached to. Instead, it refers to how many carbons are attached to the nitrogen. For amines only, primary, secondary, tertiary, quaternary refer to the number of carbons attached. The first molecule I wrote would have been an example of a primary amine, with two carbon groups, a secondary amine; with three carbon groups, a tertiary amine; and then this one is called a quaternary ammonium salt.

I haven't shown a particular counterion, but it's automatically going to be an ionic compound. Phosphorus, also in the same column as nitrogen, one of the pnictogens. {skipped over for this lecture}

Let's move on to a small sampling of the unsaturated heteroatom groups. You can form multiple bonds with halogens; it is possible, but they're more exotic compounds, so we'll just start with the chalcogens, with oxygen. Two very related groups; these are two groups that contain a carbon-oxygen [double] bond. The common name for that kind of bond itself is carbonyl. If we have a carbonyl that has a hydrogen – whether just one hydrogen, or you could have two attached – this forms the functional group aldehyde. If instead you only have alkyl groups, carbons that are attached on either side, in this case R must equal alkyl. If you have alkyl groups on either side, that is called a ketone.

If we have a carbon-nitrogen double bond, this is called an imine. So, we have amines and imines, later, we'll have amides, imides, and enamines.

There are a large number of what are known as carboxylic acid derivatives. If you take benzoic acid, for example: take the hydrogen off, put an alkyl group on, it's an ester; take the oxygen off and put a nitrogen on, it's an amide. Take that off and put a halogen it's an acyl halide. Put two carboxylic acids together, an anhydride.

In terms of naming. What if we have an alkyne, and amine, and an alcohol all on the same molecule? What do we do? There is an established functional group priority order. We look at a molecule and figure out which is the the most functional group. In terms of general classification, the ones that are at the top are these carboxylic acid derivatives. They're followed by the unsaturated heteroatom groups – things like ketones and aldehyde. Below that, we have the saturated heteroatom groups – things like [amines?,] alcohols and thiols. Below that, plain hydrocarbons. That means that means most groups are more important in terms of naming than a carbon-carbon double bond or triple bond. But below even the carbon-carbon single bond, are the halogens. That means that halogens are always considered substituents. In fact, they are named as follows: fluoro-, chloro-, bromo-, and iodo-. Fluoro- has to be one of the most misspelled word in chemistry. The other one is the molecule toluene, which is benzene with a methyl group on it.

With these halogens, let's see some examples of constructing compound names. We'll start with a simple example – one where we have two of the same kind of substituent. Taking rule #1, we find the longest carbon chain, which there's only one way to count it, so it is the hexane, going straight across. Rule number two: number to give the lowest possible number to the first substituent. Would we number this compound from the left or the right? From the left, because we're going to encounter the number 2 if we number from the left but the number 5 if we number from the right. We have two of the same kind of substituent. In proper nomenclature, we always name how many of each substituent that we have. We're going to use these multiplicative prefixes, the same ones used to name binary inorganic compounds. Mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, deca-. I put a star next to mono because we hardly ever use mono with simple types of molecules. We have two bromines: it will therefore be dibromo. They are at the 2 and the 3 position, so this will be 2,3-dibromohexane. Notice there's a comma to separate the numbers, and always between numbers and letters you use dashes to separate.

Let's look at the next more-complicated example – if you had two different substituents. We have a bromo- and a chloro- – which one should we list first? Bromo; why? Alphabetical – that b in bromo comes before c in chloro. [It does not have anything to do with the size or mass of the atom]. Rule #3: substituents are listed in order of alphabetization. 2-bromo-3-chloropentane.

Let me draw what would happen if we flipped bromine and the chlorine. Although bromine is more important in terms of alphabetization order, we number this so as to give the lowest possible number to whatever substituent that we happen to have. So, we will still going to number from the left because chlorine, although it appears later in the name, it's the first substituent we get to. So this compound is going to be 3-bromo-2-chloropentane.

Since we're dealing with just two substituents, let's handle the different case of two substituents. Now we have bromine and chlorine at what would be the same positions – the same positions meaning, number from the left you get two and four, number from the right we get 2 and 4. Which way should we number this compound? We're going to number it so that bromo gets the lower number. If we're following an alphabetization rule, that's the logic behind it. If you're having to choose, number which one comes first if numbering both ways gives you the same number. So rule #4: if numbering the chain from multiple directions yields the same set of locants, then priority is given to the substituent name first alphabetically. In this case, bromo- comes before chloro-, so we're going to name this 2-bromo-4-chloropentane.

I did not write this in a trick way. If you go from left to right, this is the maximum number of carbons, so it is a 10-carbon compound, so it is a form of decane. What kind of substituents do we have? We have alkyl substituents; what types? Methyls and ethyls. Which direction should we number this chain, from left or right? The left. Why? Because starting from the left, no matter what kind of substituent it is – alkyl groups in terms of classes of functional groups, they're all equivalent in priority – from the left, we're going to get the #2 position; from the right, 4. Regardless of alphabetization or anything, whichever substituent appears first gets the lowest number; to do that, we would number from the left. So now, what are the positions of the methyl groups? 2 and 2.

You name every substituent's position, even if it's a repeating of that number, so this would be 2,2-dimethyl-. What about the ethyl substituent? 5, 6, and 7. Since there's 3 of them, it's triethyl. Now which clump of substituents do we name first? Ethyl, why? E before m. But what about the di and the tri, isn't d before t? But it doesn't count. That's rule #5: simple multiplicative prefixes are normally not used in alphabetization. We'll see a notable exception after seeing the regular rules. The m in methyl does come higher than the 2 ethyl, so we would name this compound 5,6,7-triethyl-2,2-dimethyldecane.

Let's see an example of a functional group, starting with alcohols. We're starting with alcohols because they're easier name to alkenes. Rule #6: A higher-priority functional group receives numbering priority over a lower-priority functional group. Alcohols, if had [carbon-carbon] double bonds or triple bonds, or halogens on the molecule, you'd ignore all of them and just look at where the alcohol is to determine how you number the compound. Numbering is established by highest-priority functional group. For numbering compounds with functional groups, 99% we're only going to number the carbons. Yes, the alcohol is further on the right, but we don't label the oxygen with the number 1, we start with the carbon that it's attached two. There's two ways to show the position of the alcohol. The old-school style would be to call this 1-butanol. Notice that to make the name, we're using the -ol ending. Any alkane, drop -ane, add -ol. This is the older style, because the newer way is to put the position number right up next to what it is referring to. In that case, you'd name it butan-1-ol. This is the system used in the most recent edition of the IUPAC guidelines, but many textbooks still use the old style, many chemical names use the old style, so you should be able to read both. I prefer that you answer in the new style, but if you do it correctly, you can use the old style as well. This is for a single alcohol.

Let's get into a numbering situation between substituents and functional group. Again, the rules states that numbering is established by the most important functional group. So yes, if we number from either direction, we're going to get 2 and 4 again, but because an alcohol is more important than an alkane, the alcohol wins. This would be 4-methylpentan-2-ol.

What would happen if we had multiple alcohols? Just like we name each position of the substituents, we name each position of an alcohol. Just like we name how many substituents of the same type we have, we name how many functional groups that we have. This would be called pentane-1,2-diol. Again observe that any time we separate number and letters there's dashes, any time we separate numbers from each other it's commas. One minor spelling rule, one orthography rule: if two consonants would end up being right next to each other – we have a consonant because of this di that appears for the diol – to not have the n bump right up against the d, we leave the 2 in. But notice that with the single alcohol, we don't have an e because it's followed by a vowel; it's not used because the consonant is followed by a vowel. {question about practice problems}

Alkenes

For naming simple alkenes, how to number correctly: there are two carbons in each double bond. You number so that you give the first carbon you encounter in the double bond, that gets the lowest possible number. Numbering from the right, the first carbon of that compound gets the lowest number possible (1). If we number from the left: 4, that alkene would get the number 4. Since the number 4 is higher than 1, we stick with 1. So it is pen-1-ene. Just like with alcohols, where when there's multiple alcohols we use prefixes, for alkenes there's prefixes as well. Numbering from either direction you get the same answer. The first number for the alkenes in each case will be 1 and 7, so this is octa-1,7-diene.

What about the case of something like 2-pentene or pent-2-ene? There's no such molecule as just pent-2-ene. There's this pent-2-ene and that pent-2-ene. Once a double bond forms, it doesn't want to split apart again, so two carbons in a double bond, unless there's a chemical reaction, rotate together. So, whatever's attached to an alkene, on either side of alkene, they can't move independently of each other. There two molecules – without reacting them – are locked into these configurations.

We need to define a bit of terminology, because sometimes we're going to need to talk about what happens at the lefthand versus the righthand carbon, one carbon versus the other in an alkene, and we can use the word side. But, when we talk about reactions of alkenes, we're going to talk about in some cases things adding to just the top of the double bond or the bottom (the way that it's written on the paper); you'd also use the word side there. So that I'm always using the same word to refer to the same relationship, we're going to make this split: that if I'm talking about one carbon versus another, that yes, I'll be talking about the different sides of the double bond. Based off of the other stereochemistry terms we'll learn later on, if we're talking about the top or the bottom, we'll talk about the different faces of the alkene. So, left and right, written this way, the different carbons, those are the different sides; then, their positioning, one half or the other, looking to add to the alkene as a whole, that'll be one face or the other.

Back to these two examples: if on opposite sides you have the substituents pointing in opposite faces, they're called trans. If you have the substituents on either side on the same face, then that's cis. Trans would be opposite, cis would be same. This first molecule would be called trans-pent-2-ene, then cis-pent-2-ene. {They're on pent-2-ene} Hex-2-ene, you'd have the same thing: cis and trans. Doesn't matter how long the compound is, it's just whether the substituents are on the same face or opposite faces.

But, there's a very important point: the terms cis and trans can only be used when comparing exactly two objects. You'll see violations of this rule, but it's not following proper IUPAC nomenclature. On both of these examples, you only had two things you were looking at. What about something like this. Is this cis or trans? No, or yes, because it's both, but you can't call it cis or trans, because it's an ambiguous name. So, there is another set of symbols, another set of stereodescriptors: entgegen, zusammen, opposite, together (they're German terms). E is going to be the equivalent of trans, and Z is going to be the equivalent of cis. How do we determine which one is which? We have a system of what are called the CIP priority rules – the Cahn, Ingold, Prelog priority rules. These researchers came up with a way of naming not just alkenes, but more generally, stereoisomers, cases in which you have tetrahedral geometry. As soon as you say you have a tetrahedron with four unique substituents, there are two ways to arrange them – one that we call righthanded, one that we call lefthanded. This priority rules how do you establish what the arrangements are.

Here are the rules: 1) Higher priority is given to higher atomic number. Rule 1a) higher priority is given to higher mass number. First, you look at the number of protons, and then you look at the number of neutrons. How do we use this first rule? Let me write in the hydrogen that's on the right side of this alkene. We have a hydrogen versus carbon. Since carbon has the higher atomic number, then the chain containing that carbon is called more important. If we look at the left, the very first thing attached to that alkene, both of those are carbon, so we can't look at that first position. So rule #2 is that if priority cannot be established at the point of attachment, the next point out is examined. So on the left side of this alkene, we have only hydrogens that are attached. On the top substituent on the methyl group. On the bottom, though, we have another carbon attached. Since that carbon has priority over this hydrogens, this whole substituent ends up being higher priority. When naming with the E and Z system, the most important group on each side is identified. Since this is the equivalent of cis – the two most important groups are cis – this is (Z)-3-methylhex-3-ene. When do we use numbers with the Es and Zs? When there are multiple double bonds.

Functional groups; more nomenclature; priority rules.

Saturated – maximum amount of hydrogen attached possible (all single bonds)

Unsaturated – contains double or triple bonds (or rings)

For amines, 1°, 2°, 3°, 4° refer to # of carbons attached.

Functional group priority order: carboxylic acid derivatives; unsaturated heteroatom groups; saturated heteroatom groups; hydrocarbons; halogens (always considered substituents)

{F – fluoro; Cl – chloro; Br – bromo; I – iodo}

Multiplicative prefixes : {1 – mono; 2 – di; 3 – tri; 4 – tetra; 5 – penta; 6 – hexa; 7 – hepta; 8 – octa; 9 – nona; 10 – deca}

Rule #3: Substituents are listed in order of alphabetization

Rule #4: If numbering the chain from multiple directions yields the same set of locants, the priority is given to the substituent name first alphabetically.

Rule #5: Simple multiplicative prefixes are (normally) not used in alphabetization.

Naming alcohols

Rule #6: Numbering is established by the highest-priority functional group.

The terms cis & trans can only be used when comparing exactly 2 objects.

CIP Priority Rules (Cahn-Ingold-Prelog)

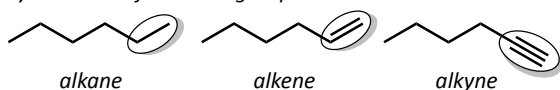
Rule #1: Higher priority is given to higher atomic number.

Rule #2 If priority cannot be established at the first point of attachment, the next position out is examined.

Structures

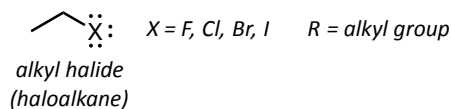
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Hydrocarbon functional groups



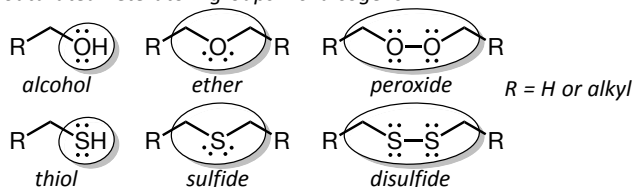
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Saturated heteratom groups – halogens

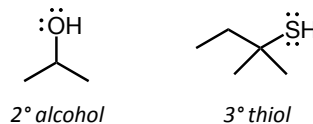


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Saturated heteratom groups – chalcogens

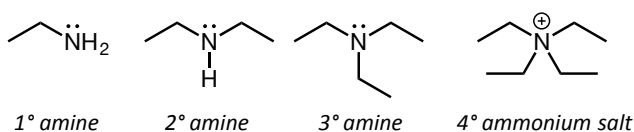


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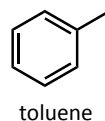


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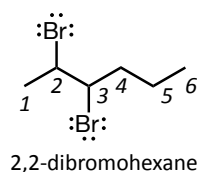
Saturated heteratom groups – pnictogens



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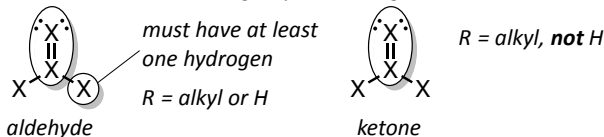
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Unsaturated heteratom groups – pnictogens

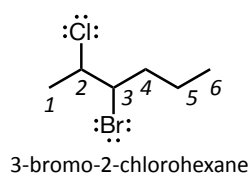
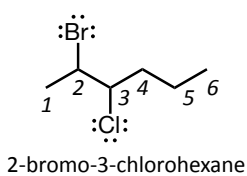


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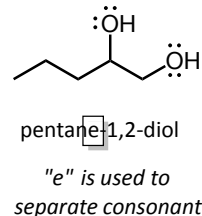
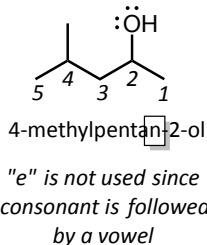
Unsaturated heteratom groups – chalcogens



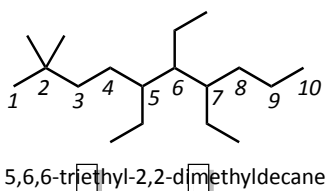
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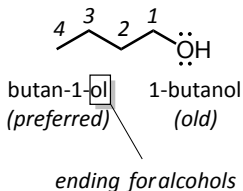
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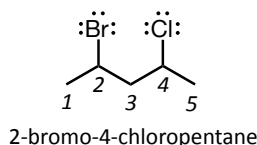
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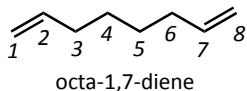
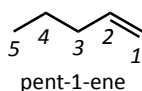
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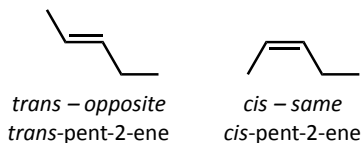
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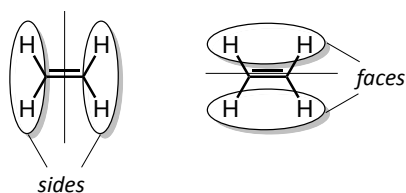
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