Lab 2A • 01/11/12

[Syllabus]
[Explanation of order of topics]
[Safety equipment]
[Chemical pet peeves]
[Chemical safety, storage (grease, labeling), and segregation]

Introduction to nomenclature of aldehydes and ketones

First, let's start with identifying the two different functional groups. Aldehydes are this kind of compound, where you have a carbonyl – a C=O bond is known as a carbonyl bond; one side or the other must have a hydrogen directly connected, that's what makes the compound an aldehyde. It is possible to have two hydrogens; that would make it the compound formaldehyde (that's a common name) or methanal. Related to this is a ketone. A ketone, however, cannot have a hydrogen directly connected to the carbonyl.

Let's start with the nomenclature of aldehydes first. Since an aldehyde is a compound that must have a hydrogen connected to the carbonyl, they are, by default, always terminal. Because of that, you don't need position numbers, you don't need locants to name aldehydes. We use these position numbers to be able to tell isomers apart, but there's no such thing as an aldehyde at the two position, for example. The functional group ending for an aldehyde is -al; you tack it on after the 'n' in a compound name. For example, this four carbon compound, that's butane, drop the 'e', it turns into butanal. Even if we had two aldehydes, again it would have to be both at the end positions of a molecule. So we could call this simply butanedial. That pesky minor spelling rule: notice that in 'butanal' there's no 'e', because, in this system, we don't put two vowels together, normally. Notice that the 'e' comes back when we put the 'di' in there, because we would otherwise have two consonants bumping into each other. This is if we just had a plain aldehyde.

What if we had some other functional group on there? Let's remind ourselves of functional group priority. Functional group priority is not directly related to reactivity, although there are some cases where the two overlap. For example, aldehydes are more reactive than ketones. Partly because of that, aldehydes are considered more important in terms of nomenclature, because there can be only one named functional group ending in a molecule. A compound may only have one primary functional group ending. That's why you'd use this set of priorities to figure out how to name a molecule. Aldehydes, more important than ketones, both of which are more important that alcohols. Part of this rationalization is that the lower priority groups are saturated functional groups, only having single bonds. Most of the unsaturated functional groups are given higher priority. Below alcohols, then we have plain old hydrocarbons, so alkanes and alkynes would be below an alcohol in priority.

Let's say we had a compound that had both an alkene and an aldehyde. In this casse, in theory, I could number the chain from either direction and have a functional group end up with the numer 1. But, going right back up to the functional priority list, an aldehyde is more important than an alkene. That's going to establish the numbering direction, starting from the right, so that we give the more important functional group the lower number. Back up to the simple aldehydes: notice that the 'n' remains in that name. [Many compounds] have that 'an' ending in there to show that they are saturated compounds. The only time it changes, normally, would be in something like this, where now we do have an alkene. Alkenes and alkynes are kinda an exception to where you only put one functional group ending; that's just the way the naming system was designed because it's so common to have double and triple carbon-carbon bonds. This is a four-carbon compound, so we start out with 'but', but it's an alkene, so instead of saying 'an(e)', we're going to say 'en(e)'. It's a the three position, so this is but-3-en. It's an aldehyde, but because it's an aldehyde we don't need a number, but we do need to say that it does have that functional group. So this would be but-3-enal.

What if we had an alcohol instead of an alkene? Same four-carbon compound, but now I'll put an alcohol on it. R or S? R, because the alcohol: oxygen is more important, a carbon with anything other than hydrogen is more important, and then a carbon with only hydrogen on it, which is the least important, other than the hydrogen that's correctly in the back. So yes, this is an R stereocenter. An alcohol is less important that an aldehyde, so we can't call this an -ol. What do we do? We turn this into a substituent. An alcohol substituent is called 'hydroxy'. There is a term 'hydroxyl', which refers to a radical. In standard nomenclature like this, the 'l', we don't us it, it's just 'hydroxy'. The hydroxy group is going to be at the 3 position, because the aldehyde establishes the numbering direction. 3-hydroxbutanal.

If we had an alkyne, it would be ynal.

I'd like to show you an example where we have an aldehyde, an alkene, and an alcohol, all on the same molecule, since it's not an entirely rare kind of critter to have. Let me comment on the double bond there: is it possible to have an isomer of this molecule where the double bond is still in the exact same position? Would the terms cis or trans be used to describe this molecule? Can I use the terms cis or trans to describe just the double bond? The answer is yes; that's trans, isn't it?

If I draw the extra hydrogens in here, it might help show that those two hydrogens are trans to each other. Yes, it's appropriate to use cis and trans here, because I only have one substituent on either side of the double bond; in other words, each carbon only has one group on it, so it would be ok to use cis/trans. I could use E and Z also. What I was originally trying to get at: yes, we need to use one of these terms because it's not a terminal alkene; there is the possibility of having another isomer of this. I can describe the bond as cis/trans; can I name the whole molecule using the terms cis/trans? That is a different question from whether the bond is cis or trans. The rule is: if you only have one double bond that needs to be specified, yes, you can use cis/trans. The whole problem with cis/trans is that you can make one and only one comparison. If this is the only comparison being made, which it is, we could use cis/trans. But, we have a stereocenter, too, don't we? We're going to have to use R and S already. To make a cleaner name, I prefer to use the E and Z, because you can lump those into the same set of parentheses that use R and S with. I prefer E and Z in general, anyways. So, is this E or Z – and this is not a yes/no question. There are times when I could ask the question: "is this E or Z?", and the answer is "no". Because, if you have a terminal alkene, it's neither E nor Z, so when I ask if it is E or Z, the correct answer is, no. In this case, it is one of the two, so is it E or is it Z? E. E is the same as trans.

What about the stereocenter, R or S? It is S, but in order to make sure you get the right answer, you have to use phantom atoms. If you have a double bond, you have to replicate the atoms in that double bond so that there's a systematic way to assign priority to unsaturated systems. In other words, if we were to rewrite the molecule in this way…. Here's everything on that molecule other than the double bond that's supposed to be there. When we have these unsaturated systems, we double whatever the bond is connected to. One carbon is doubly bound to another carbon, so we put a second carbon in to show that. It's a carbon-carbon double bond, so both carbons end up with an extra phantom carbon. How does that apply to determining the stereocenter in this case? If we look at the stereocenter itself, it's got [O, C, C] attached. We can't, from just the immediate atoms attached, determine what the priority is, so we have to see, instead, what's attached at that carbon, what's attached at that carbon. On the righthand of the two carbons, there the carbon that the carbonyl's part of, then otherwise, there's two hydrogens at that point. On the left of the carbons, because we have formally used that phantom atom, we can see that there's technically two carbons attached at that position. The way that this priority determination works is the first point of difference rule, which means you try to make your decision at that first atom that's attached. Only then if you can't figure out, then you go to the next position out. Only if you can't figure from that next position out do you keep on going. At that first position out, we can see that we have [C, C, H] versus [C, H, H]. The C in the middle here is more important than the H, and so that makes the lefthand side the more important of the two carbons. So now we have priority 1 on the oxygen, priority 2 on this lefthand group, priority three on the righthand group, and, there is the unwritten hydrogen that is correctly in the back of the molecule for visualization, so going around counterclockwise, that means yes, this really was an S stereocenter.

Let's fold all of this together into a name. It doesn't matter if it's R or S or E or Z, you list all of these different stereodescriptors in numerical order. We're going to number the compound from the right again, so this will be (3S, 4E)-3-hydroxyhex-4-enal. That'll be about as complicated of a molecule as we'll get.

Let me briefly show you the nomenclature of ketones. Ketones, you do have to name the carbonyl position, because by default, a ketone must be an internal functional group because you can't have a hydrogen on the carbonyl. We would number this in such a way to give that as low a number as possible. From the left if we numbered it, it would get number 4, from the right is we numbered it, we get number 2, so we would number this from the right. It's a five-carbon compound, so it's pent-; it's otherwise unsaturated, so the 'an' is there; and then we show 2-one, to show the position of the carbonyl. pentan-2-one. Just like we saw a common system of nomenclature for ethers, we're going to see a common nomenclature for ketones.

One step more complicated than this is what if we have multiple ketones on the same molecule. In this case, numbering from the left, the first carbonyl we would run into would have position 2; if we numbered it from the right, the first carbonyl we'd run into would be position 3, so we're going to number it from the left. It is a seven-carbon compound, so it's hept-; it is saturated, so it is 'an'; we're going to have to use one of these multiplying prefixes, since there's three carbonyls, so there's going to be a 'tri'; we don't put an 'n' and a 't' next to each other, so we're going to put the 'e' there. We need to name the positions of the carbonyls; they're at positions 2, 4, and 5. So this is heptane-2,4,5-trione.

Three more quick examples to do.

Let's throw an alkene in there. In this, we again use functional group priority. If I was ignoring functional groups, I might look at this and say: well, the alkene I could number 1, and the ketone would only receive number 2. But that doesn't matter. The ketone is more important, so that forces the numbering from the left, which yes, gives a bigger number to the alkene, but it's the less importan functional group. So this is pent- because it's 5 carbons; 4-en, because it's unsaturated; 2-one, naming the position of that ketone. pent-4-en-2-one.

What about an alcohol instead? Just as before, when an alcohol becomes the less importan functional group, it becomes a hydroxy substituent. This would be 4-hydroxybutan-2-one.

What if you had both an aldehyde and a ketone? The aldehyde is the most important functional group, so we're going to have to name this as -al. But what do we do about a ketone? How do we make it a substituent? It has the substituent name 'oxo'. This becomes 3-oxobutanal.

Oxidation reaction

Notationwise, sometimes chemists will just use an 'O' in brackets, [O], to represent oxidation without getting into worrying about which reagents are being used, just focusing on the type of reaction going on. We're oxidizing cyclododecanol into cyclododecanone, using bleach, bleach oxidation, which is a much safe set of conditions than some other possible oxidations. To demonstrate this as an oxidation, let's discuss the oxidation state of carbon, the reactive carbon, in both of these molecules. We need to review the difference between oxidation state and formal charge. What is that oxidation state? Zero. How can you get that? There is this overall rule that says the sum of all the oxidation states on a molecule has to add up to zero, so you could use the normal rules to figure out what oxygen and hydrogen should be. But I have a problem with those rules, because if I wanted to quote the way that they're expressed in [Chem] 1A: oxygen is -2, except when it's -1, except when it's 0; hydrogen is +1, except when it's not; chlorine is -1 except when it's not. Every single element you name, even fluorine: fluorine's -1, except when it's F2, and then it's zero. Why have a system of rules where it could be anything. What's the rule for carbon? Carbon can be anything from +4 to -4, depending on what's connected to it. What you really do is the following: you look at what's directly connected at that position. We use the definition of what oxidation state is. Oxidation state is treating all bonds as if they're ionic bonds, meaning that the electrons are given to whichever atom is more electronegative in that bond. Formal charge, you treat everything as completely covalent bonds, which means we would break all of the bonds homolytically to give one electron to each atom in that bond. If we did that to this molecule, broke it apart: the oxygen is more electronegative than carbon, so it would get the pair of electrons that would be in that bond. One carbon versus another, they're equal electronegativity. So, the central carbon would get one electron from each of those. Then, the hydrogen down below, it's less electronegative than carbon, so both of the electrons would come back to that carbon, if we were counting electrons this way. The real true is that there is no such thing as oxydation state, there is no such thing as formal charge; there's dipoles. These are some ways to try to quantify these dipoles, but from two different perspectives: one, an ionic perspective; one, a covalent perspective. Once we've done this breaking of the bonds in this way, how many electrons do end up on that central carbon? 4. How many electrons would unreacted elemental carbon have in its valence shell? Also four. Since those numbers match, that's why this does have an oxidation state of 0.

What if we did the same analysis on the other molecule? I'm just focusing on the carbon that's part of the functional group. Breaking it apart, it would look like this. Oxygen would get both sets of electrons from carbon; there's now a double bond, but oxygen is still more electronegative. If we have carbon versus carbon, then each carbon would retain one electron from the bond (in this counting system; none of these bond breakings really happen; this is just the way to evaluate the molecule). How many electrons end up on that central carbon, then? It's got two, instead of the four it would have as an unreacted neutral element, which means it has an oxidation state of +2, which means it was oxidized. It is an oxidation reaction.

[lab directions]

[chemical waterfall (reflux)]

The logic behind checking with starch paper is the following: you're using bleach to oxidize the alcohol. If you use up all of the bleach, how can you be sure that you've converted all of the alcohol? You let it react for a while, you test it on this starch paper. If you don't see anything happen, then that means there's no bleach, then you have to worry, ooh, was there enough bleach for the reaction to happen. We err on the side of caution and add more bleach in. You do that until, after it's reacted, you test it on your starch paper and get a positive reaction; a positive reaction means you have excess bleach, which means you had enough at least to do the reaction. Don't dip the starch paper into your reaction flasks, because the chemicals on the starch paper will get into your reaction; instead, you're going to touch a pipette or stir rod or something to the solution and then touch that to the starch paper.

[how to tell which layer is which]
[multiple extraction]

You then have a series of washes. NaHCO3 for excess acid. NaHSO3 for excess bleach.

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Aldehydes & Ketones

C=O carbonyl bond

Functional Group Priority

A compound may only have one primary functional group ending.
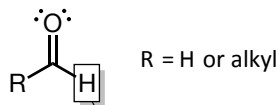
alcohol substituent –> hydroxy

oxidation

Wash

1) $NaHCO_3$ – neutralize excess acid
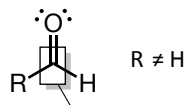2) $NaHSO_3$ – reduce excess bleach
3) NaCl – forces out ionic impurities

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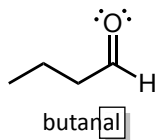**Structures**

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Aldehyde

R = H or alkyl

At least one H must be
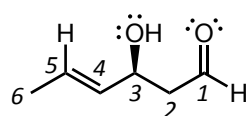connected to C=O

R ≠ H

No H on C=O

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Ketone

butanal
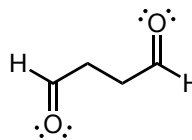
butanedial

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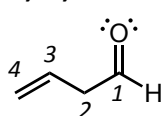
but-3-enal
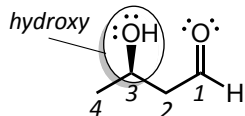
hydroxy

(*R*)-3-hydroxybutanal

(3S,4E)-3-hydroxyhex-4-enal

[C, C, H]

[C, H, H]
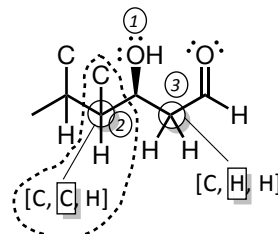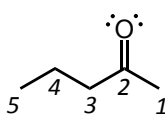
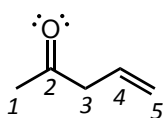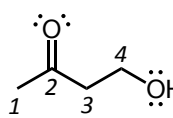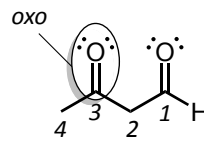*01/11/12 lab • 4*

pentan-2-one
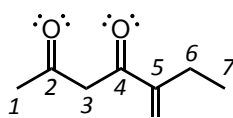
heptane-2,4,5-trione

pent-4-en-2-one

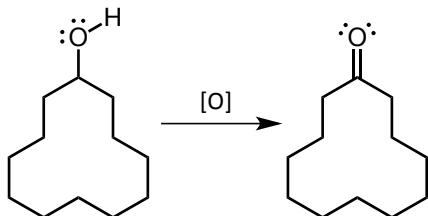4-hydroxybutan-2-one

oxo

3-oxobutanal

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[O]

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C–C–C ⟹ C· ·C· ·C

0

C–C–C ⟹ C· ·C· ·C

+2