

Lab 10A • 10/31/11

Quiz #2 problem 1 – You were asked to identify stereocenters, and you were asked to identify the configurations of those stereocenters. This problem did have, in a sense, a trick question to it, because the left carbon that has a dash on is not a stereocenter, because that position has two methyl groups on it. If you have two of the same substituent, that means if you reversed them, you get exactly the same thing back again, which means it's not a stereocenter. Only the carbon that had the oxygen and nitrogen on it was a stereocenter. The first rule that we apply is highest atomic number; oxygen is going to be priority number 1; the nitrogen's going to be priority number 2. Then we have two carbons attached – one of those two carbons only has one carbon on it, the other carbon has two carbons on it; so the one with two carbons is more important than the one with one, so this lefthand side is priority three, and the righthand side is priority 4. But, this molecule is not S because the lowest-priority substituent is currently not oriented in the back of the molecule. If you wanted to really make sure you were doing this correctly, it would have been advisable to rewrite the molecules. I'm going to rotate around the single bond here, where I'll move the propyl group into the position where the nitrogen is, move the nitrogen where the oxygen is, and then move the oxygen around where the propyl group is. If I do that, I get the following. Now we can see that the most important groups are going in a clockwise direction, so that stereocenter has an R configuration.

Next molecule. This one does have two stereocenters, because those two positions where there's dashes or wedges, there are four unique substituents, because from either one of those positions, if you go one way around the ring versus the other, you're going to get two different types of groups. The top carbon, oxygen is priority number one; we have two carbons attached; one of the carbons has carbon and two hydrogens, the other carbon has [C, D, H]. Since deuterium's a higher mass number, it beats out hydrogen, so that direction along the ring is higher in priority. Since the hydrogen's already in back, then this is R. The other stereocenter, it is the carbon that is the highest priority, so one side of the ring is more important than the other. The top has an oxygen on it, the bottom direction doesn't, at least not until you get all the way around. So, the top is higher priority than the bottom. Deuterium is higher priority than hydrogen. This looks S, but remember if the hydrogen [the least important group] is pointed towards you, you have to reverse what you see, so this is still R.

Let's do the last one. Again there's a carbon that has two of the same substituent on it, so even though it's got a wedge, it's not a stereocenter. The carbonyl, position of the carbon-oxygen double bond, that is also not a stereocenter, because it's planar. If it's planar, it is its own mirror plane at that position, so no R or S configuration is possible. Only the middle carbon is a stereocenter. In order to answer this properly, we have to use phantom atoms. For the carbon, we double the oxygen; for the oxygen, we double the carbon. Now we can compare. Three of the substituents on that stereocenter all have carbons at the first place you come to, so we're going to compare a carbon that only has hydrogens – which that's going to end up being lower – versus a carbon that has oxygens. Both of those carbons have two oxygens, so you can't decide at that point which one's more important, so you have to go one more step out. You have to go along the oxygen itself. On the righthand side, oxygen's connect to carbon; on the lefthand side, oxygen's only connect to hydrogen. The carbon on that phantom atom beats out the hydrogen, even though it's a real hydrogen, and so the righthand group is actually the higher priority. This looks S, but because the hydrogen is pointed towards you, you have to reverse what you see, so it is really R.

Moving on to the nomenclature question. This compound has five carbons in it, so it's a form of pentanol. Be careful with alcohol names. The n in pentanol never goes away. Sometimes a vowel might be present or absent, but the n from the stem never disappears. So, it is pentanol, with an n. The alcohol position is at the one position, since this is the end of the carbon chain. This is going to be pentan-1-ol, or 1-pentanol. There's two different substituents. There's a methyl, and then the deuterium has the substituent name deutero. The deuterium is at the one position, the methyl group's at the four, and because the d in deutero is lower than the m in methyl, deuterium comes first. Then, it does have a stereocenter, and it is in the S configuration. –OH group is first priority, carbon chain second, and deuterium third.

You don't use a number when you only have one stereocenter to show where that stereocenter's at. If there's only one, it's automatically apparent. For single stereocenter problems, you don't number. (S)-1-deutero-4-methylpentan-1-ol.

Enantiomers, diastereomers, epimers

For enantiomers, you could have said those are non-superimposable mirror images, which means that all of the stereocenters from one enantiomer to the other are inverted relative to each other. {error in drawing examples} Here's an example. You wanted to show a dash going to a wedge. But realized, that I wrote two of exactly the same molecule, because this molecule has three methyl groups attached to a central carbon. Since you have three of the same group, it's not a stereocenter. Even though you changed a dash into a wedge, you haven't actually changed the molecule. You needed to make sure that you definitely had a stereocenter.

Diastereomers, you couldn't just say are non-superimposable images, because that's true of enantiomers as well. You did have to say they were non-mirror images. You could have also commented on how many stereocenters changed, but you had to be really careful about how you stated things there.

Only one needs to change, so it's not two or more, it's one or more stereocenters [that change]. But you can't just say that either; you have to say not all of them change. If you just said one or more, you could have flipped all of them, and then it'd be an enantiomer. So, diastereomers are molecules in which some, but not all, of the stereocenters have inverted. You could have had an example like the following. Notice that, even though I'm using methyl groups, this does not have the same problem of not being chiral, because each of these really is a stereocenter. So it's not using methyl groups that inappropriate for showing examples of chirality; you just have to make sure there really is a stereocenter.

Epimer, that's just a subset of diastereomer. For diastereomers, that means you had to have two stereocenters at least on the molecule. If you only have one stereocenter and it's flipped, that's an enantiomer, not an epimer. Diastereomers, you have to have two stereocenters, or more, but out of all of the stereocenters, only one changes configuration.

Is it chiral or not? We had three different molecules. First molecule – you could not just say, it has stereocenters, because the last molecule also has stereocenters, but the last molecule is achiral and the first molecule is chiral. Why? Because besides the fact it has stereocenters, it has no internal mirror plane of symmetry. Saying the molecule has stereocenters is not enough; you had to then say that the molecule had no mirror plane – or, if you made the mirror image of that molecule, you'll get a molecule that's a different molecule, which that's correct, because they would be enantiomers, which means they [individually] would be chiral. Molecule one is chiral. Jumping to the end, because we do have a mirror plane, and because we do have stereocenters, that means it's meso, which means it's achiral. The middle molecule has a mirror plane also; chops right through the middle of the molecule. But this molecule is not meso, because it does not have any stereocenters. If you go from either of the positions that has a wedge or a dash, you can go around either direction, you get exactly the same thing again. It has no stereocenters; that's why it is achiral. If you said the mirror image would overlap with itself, that is true; as long as you did not say it was meso, that would have been a correct answer.

The problem we had was this: a compound that had both an anion and a radical to it. One of the largest problems with this problem – aside from not quite knowing how to do a SMOG – is knowing how to write the structure out, knowing how many hydrogens are around. Let's do the interpretation of the line structure first. How many carbons are there on this molecule? 5. For the left-most carbon, since it's got a triple bond, there's only going to be one hydrogen attached to it. For the next carbon over, since it's already got a triple and a single bond, nothing else extra goes on it. The next position over, the negative charge would be due to, for example, a hydrogen leaving but leaving without any of its electrons. But if that's involving only one hydrogen, that means there's still one more hydrogen left. Similarly, if we have a radical, that would be a case where hydrogen left with just one electron, but that again means there's one hydrogen left. The last carbon is a methyl group, and so you're going to have three hydrogens on it.

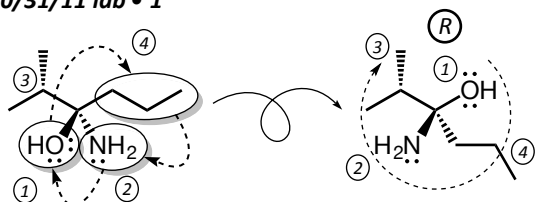
Now, how do you determine hybridization? Hybridization, we care about sigma bonds or lone pairs; individual electrons don't count, because they don't have the repulsive force; and pi bonds, since they are effectively made from one electron on each atom, they also don't have any repulsive force. So, looking from left to right, on the left, we only have two sigma bonds, so that's going to be sp-hybridization; so is the next carbon over. Since there are four pairs of electrons – three bonds and a lone pair – that means it's sp³-hybridized. The next position over, because it's a radical, there's only three sigma bonds, it's sp² hybridized. And then the last one has three sigma bonds so it's sp³-hybridized. Something that seems confusing to some of you is that a bond itself does not have a hybridization. Some of you are trying to say sp and showing the bond as sp, the bond being sp². The way that we do this model, each atom has its own individual hybridization, and all of the hybrid orbitals on one atom are the same hybrid – that's the point of hybridization, they're supposed to be the same. Where they overlap, that's a bond, and the bond's either going to be sigma or pi, but bonds don't have sp or sp²-hybridization. The first carbon, the second carbon, since they're both sp hybridized, each one would have its own pair of sp orbitals. The next carbon over, since it's sp³, that means it's going to have four equivalent orbitals. Next one over, since it's sp², that means three orbitals, and then the last one, sp³ again, which means four orbitals. Notice on each atom, there's either two, three, or four hybrids that exist, and all of the orbitals on an atom are of the same hybridization – with the one exception that the sp- and sp²-cases, we're going to have some leftover p orbitals. For sp, since only two orbitals were used to make hybrids, we have two p orbitals left over; and sp², there's only one leftover orbital; and sp³ does not have p orbitals, [since] you've used up the s and all three p orbitals, so there's nothing left. Now there's hydrogens that I don't want to forget about, and then there are two pi bonds – each of the interacting set of p orbitals on that triple bond has a pi bond – and everywhere else where orbitals directly touch, those are all sigma bonds. There's a complete SMOG for this molecule.

[lab directions] [TLC plate directions]

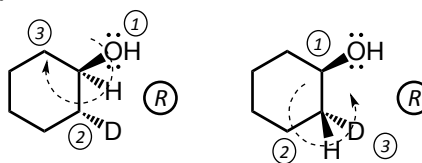
Don't use your fingers to dip the plates into the TLC mixture! Dip your TLC plate completely in, pull it back out again. Wave it a bit to get whatever stain that can drip off to get it to come off. You want to heat it for a while. The plate itself will turn a pink or purplish color. Some of your dots may turn yellow, purple, dark purple, dark blue, some of them will appear to stay white, and the fact that it doesn't have color, while the other dots do, that in itself is color information. This information may help you distinguish one compound from another, if you had multiple compounds that all have the same R_f values, but one turns yellow, on turns pink on this stain, then you can tell them apart. You should incorporate that color information into your lab report.

Structures

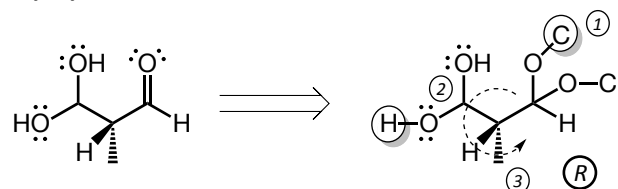
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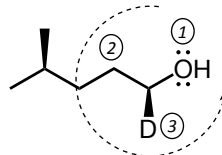
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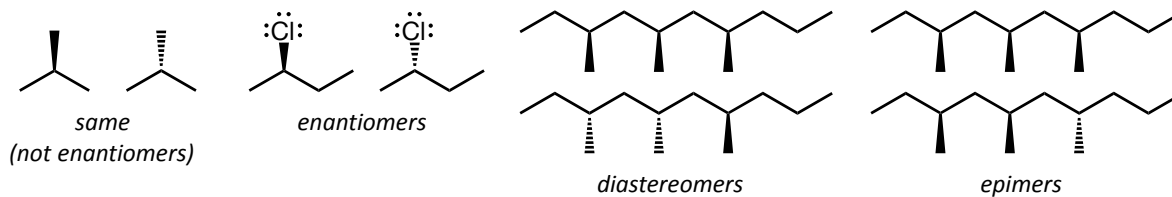


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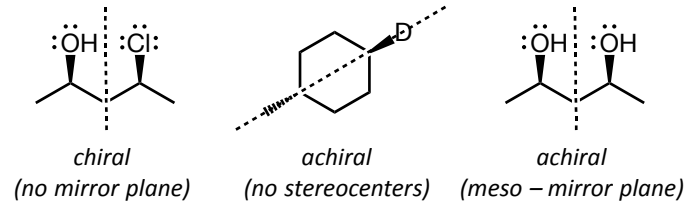


(S)-1-deutero-4-methylpentan-1-ol

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