

## Lab 8A • 05/09/12

[lab exam review]

Mixed aldols sometimes work well, sometimes don't. Let's see, in a little bit more detail, and example of a poor mixed-aldol condensation. If we had, for example, propanal and ethanal. They are so similar to each other in structure that there's not an appreciable enough difference in the pKa values that we would be guaranteed of converting one versus the other into an enolate if we use something like sodium hydroxide, which reversibly forms the enolate instead of irreversibly. In other words, even if the mixture's not exactly 50/50 of what we're going to end up with, it's close enough to 50/50 that we'll just consider it that way. In a similar way that these compounds are not all that different in their acidities, they're also not all that different in their reactivities, so once we form the enolate, it's virtually equally likely that the enolate will attack propanal versus ethanal.

I'm going to do this in a column format, where I'll show the first enolate reacting with propanal or ethanal, and then the other enolate reacting with propanal and ethanal. From the first column, we're going to get two products. Since propanal had made the enolate to begin with, propanal reforms itself. We have a double bond between the alpha and beta positions, because this is an aldol condensation. One of these we're going to add a total of three carbons, the other one, we add a total of two, so there's two of our possible products. From the other column, we get another set of products, cause here it was ethanal that made the enolate, so ethanal reforms. Again we get a double bond. Notice this time there's no methyl group also at the alpha position as we had with the first two compounds, so these four compounds are distinct from each other, and since there's not enough of a difference between ethanal and propanal, we can oversimplify and state there's roughly the same proportion of each of these enolates in solution. We've seen what can go wrong, where we get multiple products out.

Now let's see the example of where we have more control, where we do get largely just one product in our mixture. Our starting materials were acetophenone and p-anisaldehyde. Why [is] this combination an example of an ideal aldol condensation? How many types of alpha protons are there between the two compounds? Only one, because in the p-anisaldehyde, the alpha position has no hydrogens. Only the acetophenone has alpha hydrogens, and only on [one] side. Only one reagent is able to form an enolate. That cuts in half the number of possible products right there. The top case, we had four products because we had two potential enolates, and each one reacted with two potential compounds. Here, we're only going to make one enolate, so at worst, we're only going to get two products. But it turns out, we only get one. Why? Because aldehydes are more reactive than ketones. We've covered carbonyl reactivity from two perspectives up to this point: one is the reactivity of the carbonyl itself. Why is there a difference in the reactivity of the carbonyls? Hyperconjugation. If you have alkyl groups attached to the carbonyl, those alkyl groups by their sigma bonds are able to hyperconjugate, cause they're in the right geometry. An aldehyde automatically has at least one hydrogen on that carbonyl. That carbonyl's pi bond is going to be perpendicular to that hydrogen, which means it's unable to help stabilize it, which means it's more reactive. Remember that that exact same logic of electron donation into the carbonyl is what we also use to explain why certain alpha protons are more or less acidic. Since the aldehyde has less stabilization to it, it is more reactive – it's enough more reactive that the enolate is likely to only attack it, not the ketone, which is why we only get one product.

We put the two of these together in sodium hydroxide, which is not basic enough to irreversibly deprotonate, but it is good enough to get the acetophenone to deprotonate. Since acetophenone is the compound that forms the enolate, it reforms afterwards. We have a new alpha,beta unsaturation at that position, which is connecting to the anisaldehyde, so para to that second benzene, we have an OCH<sub>3</sub> group.

[IR determination – change in conjugation causing shift in frequency]

[Robinson annulation]

In a Dean-Stark apparatus, what you have is, in between your reaction flask and your air or water condenser, you have this piece of glassware that allows some of the liquid to flow down the sides as it's refluxing into that sidearm. That sidearm, you end up with an accumulation of two things: water and an organic mixture. Toluene was the main compound you used as a co-solvent, so you have toluene that could come across, and you have water. Water's more dense than the toluene, so it settles to the bottom. Water is not soluble in toluene; however, in the vapor phase, the two can move together. That is this term azeotrope, which is a gaseous mixture that phase-separates upon condensation. This is sometimes exploited, for example in isolating some plant component. [steam distillation of eugenol from cloves] Eugenol's not soluble in water, but it forms an azeotrope with water, which means it can be pulled over in the vapor phase, but then once it condenses again, it separates into two layers. That's exactly what's happening in this situation here, where water's being pulled off with the toluene, and then it separates out.

Why do we do this in the first place? Because one of the products of this condensation is water, and since this condensation is a cationic mechanism – which means it's technically fully reversible, we want to drive the reaction forward by removing water. As this reaction occurs, the reflux occurs, toluene and water reflux, and some of it gets stuck on the side here – that water never re-enters the reaction flask. If it never comes back, it means you're removed the product.

Equilibrium is when you have equal rates of the forward and reverse reactions – take out the product, you never have the reverse reaction, you only continually have the forward reaction, which is why you drive the reaction to completion. That's using Le Châtelier's principle, that's why this apparatus is used.

As a follow-up, in large-scale reaction, as the solvent builds up, it simply spills back into the reaction flask, which is perfectly fine. The water, if you let it go too long, can build up, but if you monitor the reaction, you could empty the water out to permanently and truly remove it from the reaction mixture, and you could see how much water you've got and calculate how much the reaction has completed. This piece of apparatus is called a Dean-Stark trap. We forced the equilibrium to the products by removing them as they're formed. It's not reversible because we take the water out.

[lab 3]

Answers to exam 1

[final curve][it's easier to ask for forgiveness than permission][adam ant]

Here are the retrosynthesis problems. You had the number of molecules you were supposed to use to synthesize these, and in two of the cases you had the type of functional group you were supposed to have. First problem: alpha,beta-unsaturated ketone – aldol condensation. To reverse an aldol condensation, chop at the alpha,beta position. The side of the double bond that's near the carbonyl used to be the alpha hydrogen, so you just erase the double bond at that position. The other side, that was the carbonyl that got attacked. If we number the positions, one carbonyl would be at position 1, the other, 6. There's a total of 10 carbons, so to put two carbonyls at 1,6 positions from each other, that's the [reactant].

Second problem: delta-carbonyl compound – Michael addition. If you look at the two carbonyls, one is delta to the other – that's the telltale sign of a Michael addition. How do we go backwards from a Michael addition? A carbon-carbon bond is still formed between the alpha and beta positions, it's just we end up with a single bond instead of a double bond. It turns out there's two ways to do it: I could break at the alpha,beta bond for the first carbonyl, or I could break at the alpha,beta bond for the second carbonyl. Whichever one has the alpha proton was not unsaturated; the other side of where you break the double bond, that's where the double bond. If I broke the left one retrosynthetically, what I'll end up with is acetophenone and propenal – that's probably the combo I would use, because even though the acetophenone is less acidic than an aldehyde would be, we don't have a proper alpha proton here because we have a double bond at where the alpha position is. I would have also accepted the other answer, which would have been ethanal and [some compound].

Third problem. You were told that the starting material is an ester, so you might think: Claisen condensation. But, a Claisen condensation makes an ester – if you start with two esters. What's to say you can't take a ketone and attack an ester? In other words, if you break this carbon-carbon single bond, wouldn't this compound have worked? We take the alpha hydrogen right there and deprotonate it, which starts off like an aldol condensation, but then it attacks the ester right next door, kicks the alkoxide group out, restores the carbonyl, and gives us the product. This is not a bridgehead position, so there's no reason it can't be deprotonated.

Last one of these: carboxylic acid from a ketone. Haloform reaction – iodine or bromine or chlorine, and sodium hydroxide, basic alpha halogenation conditions, which is what gives you the haloform reaction.

Let's move on. This is the malonic ester synthesis. Let's analyze this. This should be viewed as an alkylated version of acetic acid, because that's what the malonic ester synthesis gives you. The malonic ester itself, it doesn't matter what R group you had on the ester, but you needed to have this dicarbonyl compound. What is the pKa of the alpha proton on that compound? 13. What's the pKa of water, roughly? 15. That means that hydroxide is more basic than this enolate gonna be. That means if you titrate the enolate with hydroxide, you won't saponify [also anion makes attack of the carbonyl less likely] If you want to avoid any problems, then the safest reagent of all is ethoxide, if you have an ethyl ester, because the worst that happens is ethyl ester and ethoxide make an ethyl ester, make the same thing again. One way or another, we deprotonate this. We make the enolate, we react that with the appropriate alkyl halide, which in this case is aspartyl bromide [or chloride, iodide, tosylate] – triple bond with a single carbon in between the triple bond and the halogen. That will undergo Sn2, it gives us the number of carbons in the right places we need. If we had a double bond instead of a triple bond, we might have to be more careful at this next step, because if I had a double bond and I showed acid and heat, you have to worry about whether that double bond's going to react. Triple bonds are not as susceptible to plain hydration as double bonds are. If you wanted to be super-safe about it, we saponify first, and then, with a little gentle acid and heat, we carboxylate, which means we get the product.

Mechanisms

First one was pentane-2,4-dione reacting with propenal. Only one of these compounds has an alpha proton, so you know which one's going to form the enolate. We had sodium hydroxide.

The question said there's excess, which isn't really necessary, because we use hydroxide to deprotonate here, but later we use the water that's form to get attacked, which is going to make hydroxide again; the [excess] was just to give you a hint of something I'm going to show you in a moment. Form the enolate [didn't need to show delocalization]. Once you make an enolate, it reacts. Yes, it's a Michael addition. Why? Because the pKa of that diketone is only 9, which means it's a strong acid compared to water, which means this enolate is not as basic and it's heavily delocalized, so it's squishy. So since we have the soft, squishy base with the delocalized, squishy aldehyde, that's why we get a Michael addition. Initially, we're going to have an enolate. We have water from the hydroxide, which we could use to let the enol turn back into an aldehyde, which then gets deprotonated, because if equilibrium can happen, it will have – which means we have the Robinson annulation. We have what will be the beta-hydroxy group, except we need to neutralize to get there. This is going to further react, because again we can deprotonate the alpha position, which means we can undergo E1cb elimination to form our cyclic, alpha,beta-unsaturated ketone.

Second mechanism. Protonate and open [combining resonance]. Water was your other reagent, along with sulfuric acid and heat and time. That time aspect was trying to communicate to you a hint. Now we've done attack, which means we need to deprotonate. That was the first round of protonate-open-attack-deprotonate; now we go through the second round of protonate-open-attack-deprotonate. Protonated the methanol portion, [open and attack as one step]. I end up with a protonated carbonyl, that's going to deprotonate – which since you just made a beta-ketoacid, in acid and heat, is going to decarboxylate. That much time under heat and time is going to decarboxylate. In this case, it means we make an enol, which can become protonated at the double bond, reforming the carbonyl that then gets deprotonated; that is our product.

[Fill-in-the-blank]

First problem. We had acetic acid reacting with an excess of isotopically labeled water and sulfuric acid and heat. The product is also going to be acetic acid, but both of the oxygens replaced with 18-O. This is that tetrahedral intermediate. It's not just one oxygen or the other that gets substituted, because there is an excess of the 18-O, so both of them are eventually going to react.

The second one. [must keep two reagents distinct for selective reduction] The correct reagent for this one is the lithium triisopropoxyaluminum hydride [correct alkoxide?], not DIBAL-H. Acyl halides, if you used lithium aluminum hydride, the first hydride turns it into the aldehyde, but you still have more hydrogen around, and you can't stop the reaction; it'll go to an alcohol.

Next one. We have something that reacts with first a Grignard reagent, but two equivalents of it, followed by aqueous dilute sulfuric acid. The product we get is an alcohol. If we analyze this in reverse, here are the two ethyl groups that got added in by the magnesium bromide. We have some kind of four-carbon starting material that had a carbonyl in it. That carbonyl can be part of either an acyl halide or an ester. The two answers that were acceptable were this acyl halide or an ester made from butanoic acid. [A] carboxylic acid itself is not the right reagent, because you would get a ketone out of a carboxylic acid instead.

Next one. We have acetic acid reacting with this compound, which is diazomethane. It is the one basic reagent that we can use to make esters – specifically, a methyl ester.

Next problem. Acetone reacting with something to make alpha-bromoacetone. The right conditions here: acid and bromine – in other words, acid alpha-halogenation, because base halogenation would give you acetic acid, it would do the haloform reaction. We only have monosubstitution. Remember that under acidic conditions, each successive reaction is less favorable because of the electron withdrawing effect of the bromine. It's only under the basic version that that electron withdrawing effect causes it to further react.

Next one. We have something reacting with a deprotonated thiol to make a thioester. Oxygen and sulfur have similar reactivity. The best starting material for this: an acyl halide. React it with water, you get an acid; react it with an alcohol, you get an ester; react it with a thiol, you get a thioester.

A lactam being reduced by lithium aluminum deuteride, followed up by dilute aqueous acid. The ring maintains itself, but since it's a deuterated reducing agent, we do have deuterium that show up in the product. There's no source of hydride here.

Last three problems. This one hopefully screamed enamine at hour. React it with something in order to make an alpha,beta-unsaturated ketone – which means it looks like an aldol condensation. The enamine can be used to do aldol style condensations. The main reagent you use could be an aldehyde, or an acyl halide (for acylations). Technically, it's a 1/2 reaction, because the enamine doesn't go away until you hydrolyze it.

Next one had two answers [faulty question]. If you look at this product, it's a beta-ketoester, which is the product of a Claisen condensation, or since this is intramolecular, a Dieckmann condensation, which means the answer I was looking for was this: 7-carbon carboxylic acid that's actually a diacid, that's actually an ester.

You did need to make sure that both esters were the same, meaning they're both isopropyl, so that you can avoid transesterification. But, what about this other answer? I didn't tell you what the starting material had to be. An acyl halide will certainly react with this to make an ester.

Sodium borohydride reduction. This is not a diester, it is not an anhydride; it's an ester and a ketone. Notice that there's a carbon between the oxygen and the carbonyl at the bottom. Aldehydes and ketones are reduced in sodium borohydride, esters and acids and so on are not. So the product is this.

[binary]

The order of carbohydrates is totally arbitrary. There is no reason you have to list the sugars as allose, altrose, glucose, mannose, galactose, idose, galactose, talose. Why was it done that way? We need to revisit this idea of d and l sugars.

We're going to cover the five ways we can describe carbohydrates: whether they're d or l configuration; whether when they cyclize are they in the alpha or beta form; when they cyclize, do they make a five- or six-membered ring; are they ketones or aldehydes to start with; and how many carbons do they have?

Why are the carbohydrates arranged the way that they are? Recall that to call something a d sugar means the last stereocenter is on the righthand side. We have three remaining stereocenters. Each stereocenter has the possibility of the -OH group being on the left- or the righthand side. I can put these in any order I want to, but [it is logical] to say: if that bottom stereocenter's on the righthand side, let's start out with their structure where they're all on the right. [One] could call talose the first one and then go backwards through the pattern. The reason I presented this this way is the following logic: each one of the positions, the -OH group is either left or its right. Binary is a counting system where each digit is either one thing or the other; it's either zero or one. Since, arbitrarily, we start with the one where they're all on the righthand side, and counting forward that way, I defined the righthand side to be zero, in terms of numbers. There's no other reason for it than that; there's no chemical reason, no physical reason; it's just that if you have three stereocenters, [there are] eight different sugars, there's a binary pattern to it [demonstration of switches]. If I choose to read the number this way, from left to right, view the molecule that way, and if I define the righthand side of the Fischer projection as zero, then this sugar that I wrote would be represented in binary by the number 0 [0000]. Flip the top group, which the last digit in my number, that's the same as saying 1; then the next one would be 2, 3, 4, 5, 6, 7. The binary numbers 0 - 7 happen to find some connection to the structures of the sugars, if you order the sugars in this way. Naturally, geometrically, mathematically, this is a binary system, so that's why I laid out the sugars in the order that I did. Once you know the pattern, if you know the order of the names, then you could take that name, figure out which which number goes with it, and from that you know the structure.

In red, I've written the decimal number; in blue, I've written the binary number. If, in binary, the first molecule is representing the number 0, then the second molecule is representing the number 1. If I give you eight objects and say: look at the sixth object, I'm talking about binary #5, because I'm starting with the number 0. When and if we arrange the numbers in this way, and when and if we interpret them from the bottom up to mean [right, right, right, right], or [right, right, right, left].

These are all the aldohexoses that you have to memorize. There are five things about a sugar that we need to know. We need to know the number of carbons. Galactose [7th, binary 6, {0110}, [RLLR]]. This is going to make a cyclic sugar. This is in its d form - why? Because the bottom stereocenter is to the right. We have the number of carbons - this is a hexose; as the name sounds like, six has to do with the number of carbons, six carbons in that compound. What's the functional group? An aldehyde, which is why it's called an aldose, instead of a ketose - one refers to aldehydes, and refers to ketones. There's which enantiomer this is; I've currently written the d form - it's the d versus the l form, as far as which enantiomer of the sugar we have. There's two more classifications that we can't determine here, because they only happen when you make rings. There is the anomer that's formed - whether it's alpha or beta - and then there's the size, five- versus six-membered ring. Since we're starting out with linear compounds, let's start out with these first three concerns.

Functional groups

An aldose means that you have an aldehyde; a ketose means you have a ketone. If I had, for example, d-glucose [0010, RRLR, 3rd]. That is an aldose because it has an aldehyde. Let's see a close cousin of it. There happens to be an identical configuration of the bottom three stereocenters; that's not on accident, because this first sugar, which is d-glucose, can be converted into this other sugar, fructose. What is the relationship between these two compounds? Look at the top of glucose. If I were to protonate and open up the carbonyl and remove this hydrogen where my pen is, then I end up with an -OH group, and -OH group here, and a double bond between them - in other words, a "double enol", an enediol. You might then go backwards, but instead of forming the carbonyl here, I form it here - that's how I get fructose. Fructose is nothing more than the double tautomer of glucose, which means in water, they can be converted between each other.

aldose - aldehyde; ketone - ketone

Number of carbons. [Hexose] Notice that you can combine turns: aldose + hexose give us aldohexose; pentose (five carbons); tetraose [four carbons]; triose [3 carbons].

Let's look at the aldopentoses. The top and bottom carbons are not stereocenter; that leaves us three carbons that are stereocenters. The bottom one of all of these is going to be d, because the other ones are going to be enantiomers. That leaves only two stereocenters, which means there's four of them (d-aldopentoses). There are binary [000, 001, 010, 011]: ribose [deoxy means take an oxygen off of ribose], arabinose, xylose, lyxose. [source of names]. Aldotetroses, there's only two unique ones, because there's only two stereocenter, and if we're talking about the d sugars, that means the only difference between these is what the top stereocenter is doing: erythrose, threose. There is one aldotriose, which you already know the name of: glyceraldehyde.

d/l

Glyceraldehyde, there's this whacky coincidence, this lucky guess that Fischer made [where he] put the group here, call it the d form, call it the + form. The two happened to be the same in that molecule, but that wasn't known until [approaching a century] later. He was right, so we still follow that system. D means that last stereocenter's on the right; l means the last stereocenter's on the left. I'll write d-galactose again, and let's write l-galactose. What's the difference between d-galactose and l-galactose? What is the stereochemical relationship between the two? They're enantiomers, which means we switch everything. Easy mistake that people make is they focus on what d and l means, which yes means what is the configuration of that bottom stereocenter. But, d and l sugars are enantiomers, so it doesn't mean you just flip the bottom one; it means we name it, based on the bottom one. The bottom one here is on the right, which is why we call it d. The other one has all of the stereocenters inverted, cause it's the enantiomer. This is l-galactose. It's determined by the stereocenter that's furthest from the anomeric position. More simply put: determined by the last stereocenter. The d form is on the right, the l form means it's on the left. From the d to the l form, we flip everything.

Ring size

[furan, THF]pyran, DHP] Why these names? That galactose is able to form a hemiacetal, intramolecularly. If we take the position of the carbonyl and count 5 or 6 – if it grabs one of these or the other that I've circled, the -OH groups, and we cyclize, we could make a five-membered ring or a six-membered ring. If we make the six-membered ring, the structure's going to look like this. Every carbon's got an -OH group; the anomeric position's got two oxygens attached; every other carbon has one. That top stereocenter, is it R or S? Let's rewrite the carbonyl as phantom atoms. To do phantom atoms, you take what's connected to the carbon, double it; take what's on the other side of the carbon, and put a carbon on it. Which of these substituents on the stereocenter is most important? The -OH group, because oxygen's the highest atomic number. What's the least important? The hydrogen. Between the other two groups, we have to decide, because they're both carbons. Which one's more important? Once we expand using phantom atoms, we see that the top carbon's got [O, O, H] attached to it; we see the bottom carbon has [O, C, H] attached to it. Since the top has an oxygen, in comparison to the bottom one having a carbon at that point of comparison, the top is priority number two, the bottom is priority number 3. So, 1 on the right, 2 on the top, 3 on the bottom. Which way am I rotating? S. But the hydrogen is pointed towards you, because by definition of the Fischer projection, anything on the sides is facing towards you, which means whatever you see if backwards, so it's really R.

Because they're sugars and because they're making either hemiacetals or ketals, then [there is] an oxygen in the ring, which means they're both similar in character to furan and pyran, which is why the five-membered ring is called the furanose form, and the six-membered ring is called the pyranose form.

beta-l-galactopyranose. The fact that I say 'galactose' tells us which sugar it is, which also tells us how many carbons are in it: 6. Pyranose means six-membered ring; l tells me which enantiomer; beta tells me which epimer. How do we get there? We already drew linear l-galactose; we start with that. I know I want to cyclize using that last stereocenter's oxygen, cause that's going to get me a six-membered ring. Where I draw that oxygen in this ring does not matter. In real life, the molecule doesn't look anything like this, because the way that it looks like is: here's five atoms, oh yeah, there's somehow there's one atom that somehow makes this bond that goes all the way back behind here and it comes all the way back up top. The oxygen [is actually] exactly in between the top and bottom carbons, so it doesn't matter where I right it. In order to do any visualization correctly, in order to determine alpha and beta correctly, I need the compound, with the ring, in one axis of perspective. I'm going to put in some of my functional groups, some of my stereocenters. They don't change from above, but I make a new stereocenter – I want the beta form. Without some practice, I can't put that new -OH group down yet, because it's supposed to be cis or trans to the CH<sub>2</sub>OH. How can you correctly determine cis and trans if it's right in the middle? That's because we're not viewing this ring correctly, this ring goes twisting off to the side the way that we have it represented. We rediscovered how I could do this precession of groups in order to get the ring the way I want it. We [previously] rotated that last carbon the other direction – why? Because we were doing it to a D sugar. This is the l sugar, so you twist it the other way around. Remember, you want the ring up and down, twisting that oxygen down, so it's straight up and down. The other stereocenters remain unchanged. Now I can see where is that CH<sub>2</sub>OH group. Beta means the anomeric hydroxide is cis to the ring; alpha would mean the top group is pointed in the other direction. We let it fall on its side, and then we bring the substituents around so that they're evenly spaced in a hexagon.

If you do this visualization the same way every time, then what's on the right of the Fischer projection is on the bottom of the Haworth projection. We write molecules like sucrose, table sugar, we're going to find out that that's a combination of two cyclic sugars, and without doing some funky drawing there, we can't write both of them in their proper Haworth projection form. If you draw it the standard way, yes, what's on the right is always down below. On the right, since I have [-OH, -H, -OH, -OH, rest], then on the bottom, I'm going to have [-OH, -H, -OH, -OH, rest].

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1) aldol condensation – mixed aldol

Example of a poor mixed aldol

Example of an ideal crossed-aldol condensation

- Only one reagent is able to form an enolate
- Aldehyde much more reactive than ketone

2) Robinson annulation

azeotrope – a gaseous mixture that phase-separates upon condensation

- # of carbons (hexose)
- functional group (aldose)
- enantiomer (D)
- anomer (alpha, beta)

hexose – 6 carbons; pentose – 5 carbons; tetraose – 4 carbons; triose – 3 carbons

aldose + hexose → aldohexose

aldopentoses

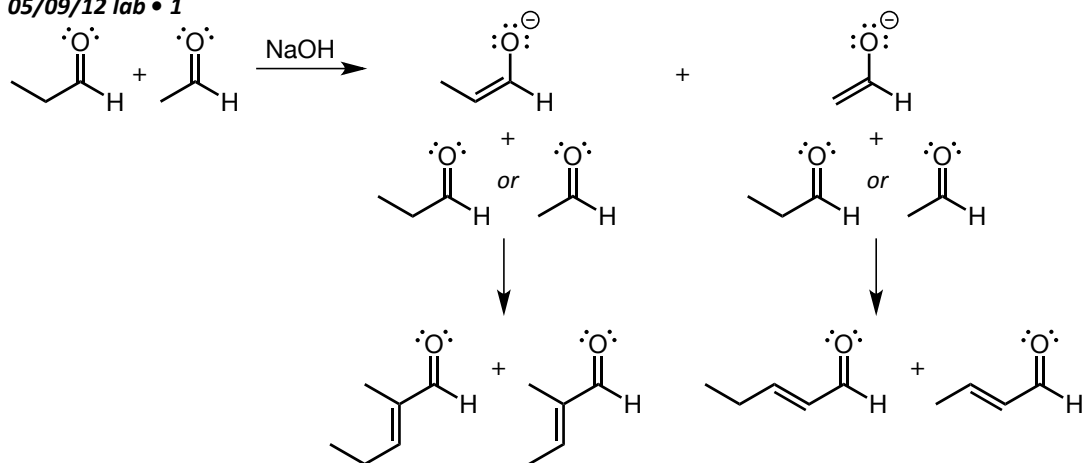
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aldotriose

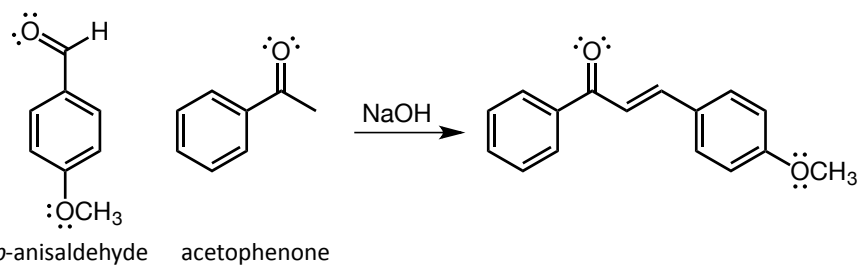
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Structures

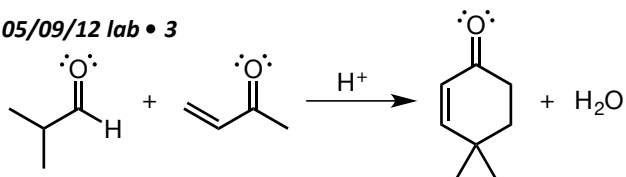
05/09/12 lab • 1



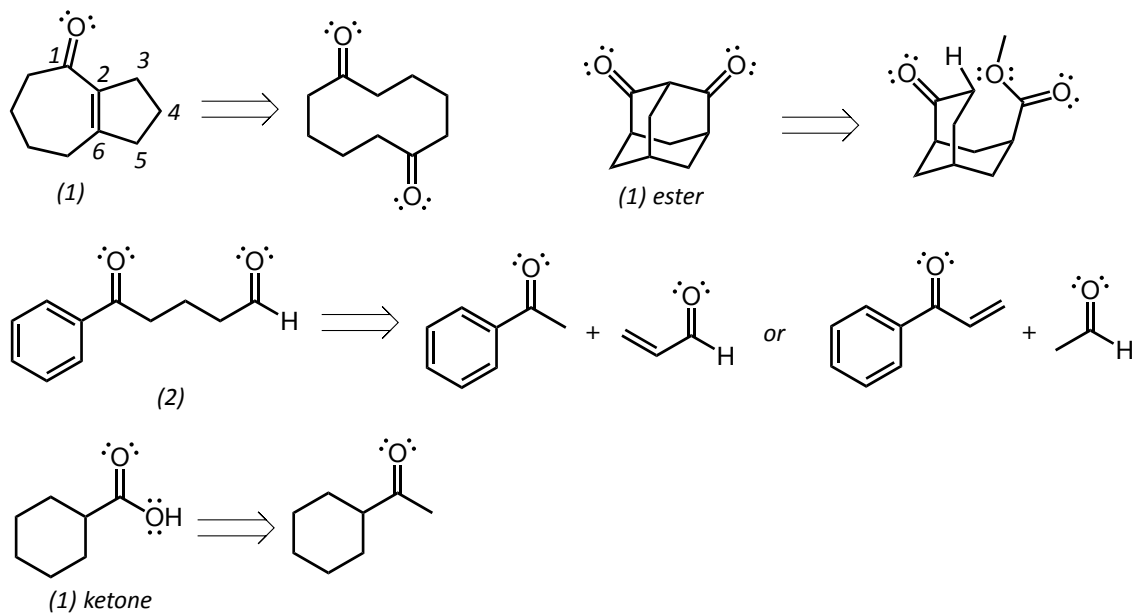
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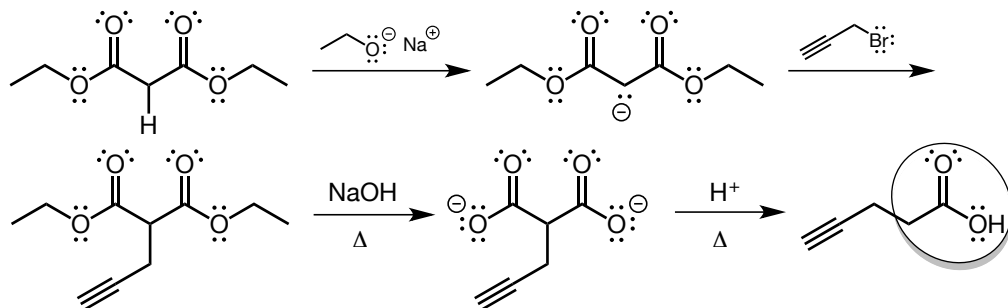
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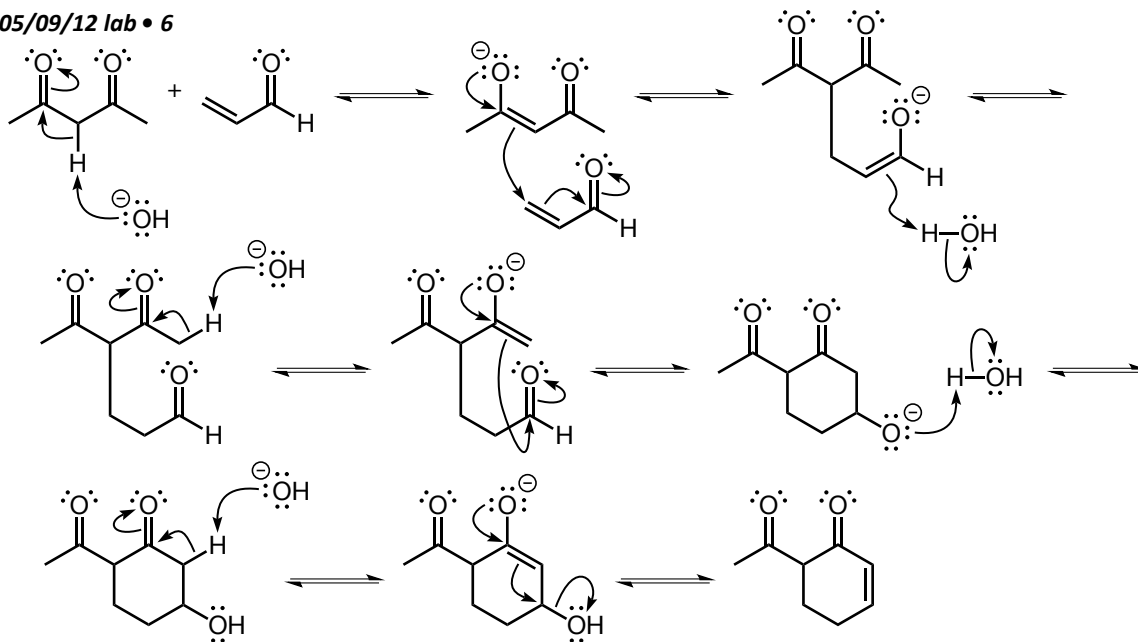
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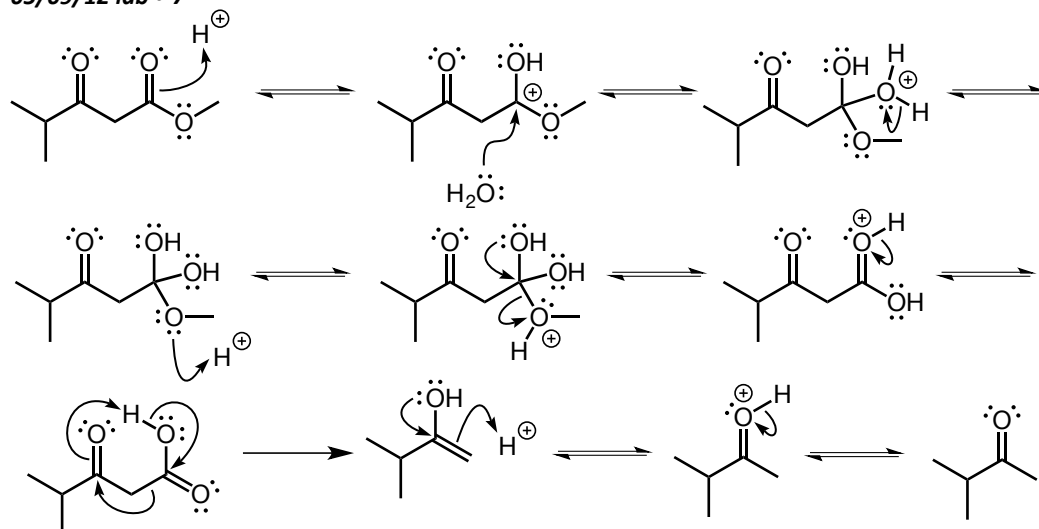
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05/09/12 lab • 6

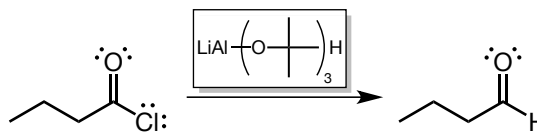
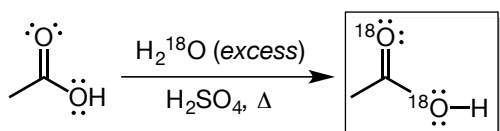


05/09/12 lab • 7

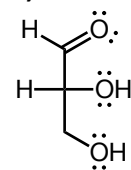
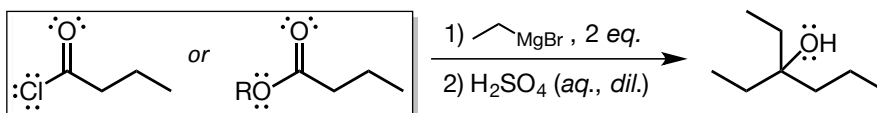




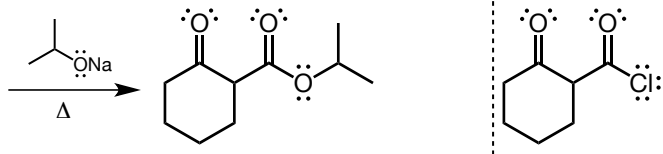
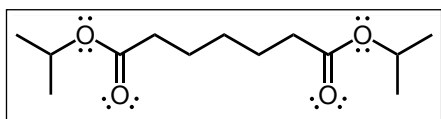
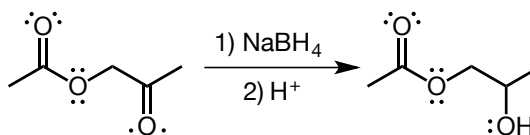
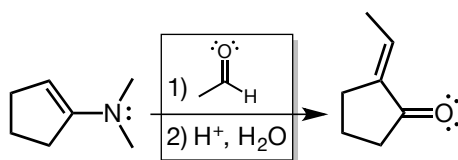
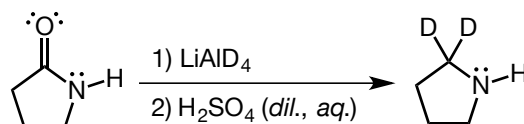
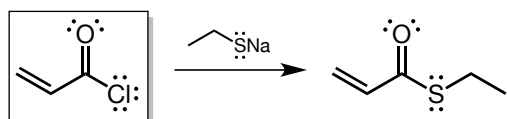
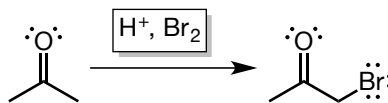
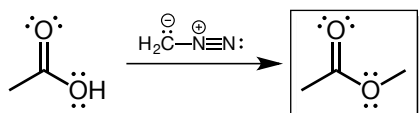
05/09/12 lab • 8



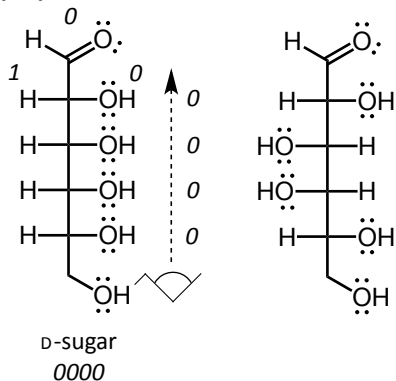
05/09/12 lab • 13



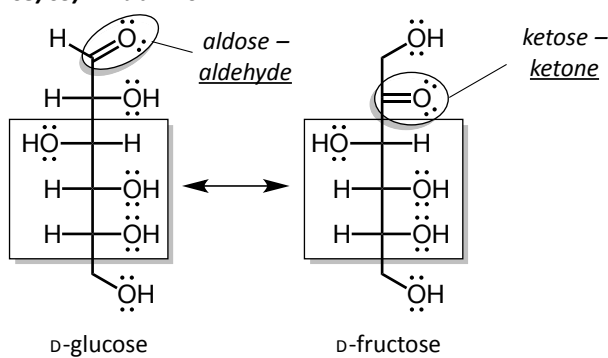
D-glyceraldehyde



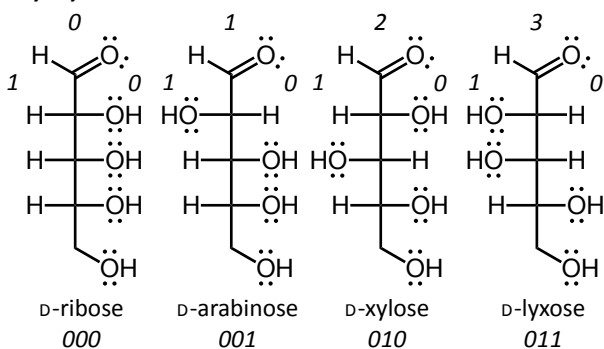
05/09/12 lab • 9



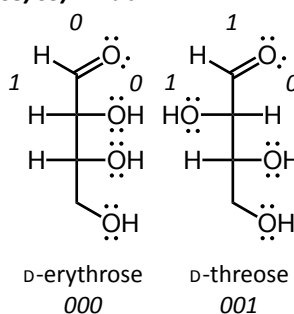
05/09/12 lab • 10



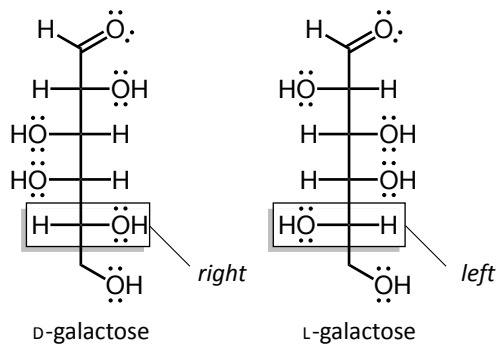
05/09/12 lab • 11



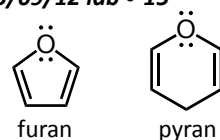
05/09/12 lab • 12



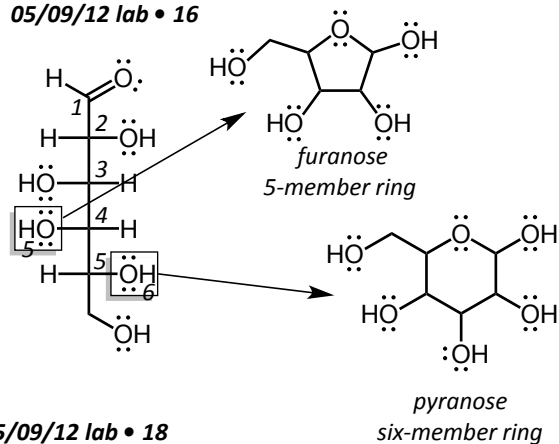
05/09/12 lab • 14



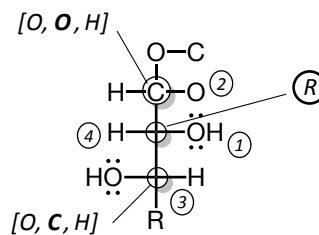
05/09/12 lab • 15



05/09/12 lab • 16



05/09/12 lab • 17



05/09/12 lab • 18

