



Carbonyl Chemistry

Transcript

Instructor: Jay

00:00:00:00 - 00:00:15:78

Instructor: Let's look at carbonyl compounds. A carbonyl group consists of oxygen atom that is double bonded to a carbon atom. As we know, oxygen is more electronegative, so it's going to pull the electrons towards its electron density towards itself, creating a partial positive charge on carbon and a partial negative charge on oxygen.

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Instructor: As a result of this, this makes a bond. This polarizes the bond. And makes it susceptible for nucleophiles to interact with carbon and electrophiles to interact with oxygen.

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Instructor: Let's look at some of the key reactions that carbonyl compound can undergo. Let's start with the hydration reaction. As you know, hydration happens two ways, base catalyst hydration or acid catalyst hydration.

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Instructor: Both the compounds will give the same final products, but the mechanism can slightly differ between them. Let's take acetone, for example. If we start with the acid catalyst hydration, the first step I would look at is, is the compound a nucleophile or electrophile?

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Instructor: Since hydrogen is electrophile and oxygen is a nucleophile, it would attack the hydrogen and protonate itself. This results in an intermediate being formed, where oxygen is going to have a partially formal positive charge added to it. As oxygen has forming a positive charge added to it, it makes a carbonyl carbon more electrophilic and more susceptible for a nucleophilic attack.

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Instructor: The next step would be the oxygen in the water molecule would attack the carbonyl carbon forming a tetrahedral intermediate. With this attack, it's going to break the Pi bond and release the positive charged oxygen. The final step would be the regeneration of the catalyst.

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Instructor: For since the water molecule now, which is attached to the carbonyl carbon atom has a positive charge, it's going to remove or deprotonate one of its hydrogen to become more stable. It results in the formation of the hydrogen ion back into the system. The final product form is known as a geminal diol as it contains two alcohol groups in the same carbon atom.

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Instructor: This is what happens when acetone reacts with acetone's hydrogen in acidic conditions. If you take the same acetone molecule and react it in basic conditions, would the final product be the same or would the mechanism differ? We are going to take the same acetone molecule.

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Instructor: Now we can react it in basic conditions. Now, as a catalyst is a nucleophile and not electrophile, the starting mechanism would be different. Previously, the oxygen protonated itself because it was an electrophile.

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Instructor: Since it's a nucleophile, the first step would be a nucleophilic attack in the partially positive carbonyl carbon by the hydroxide ion. This attack is going to cause the Pi bond break and oxygen to obtain a lone pair, getting a formal negative charge. Since oxygen is now not having a complete octet, it's going to try to be completed.

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Instructor: So as there is a water molecule in the vicinity, it's going to strip a proton from it to become complete. It's going to target the water molecule. Sure. It's going to remove

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Instructor: the hydrogen away from the water, resulting in the formation of an OH group and a geminal diol. Since oxygen now has a formal negative charge, it needs to share its electrons. So, it's going to go after the closest proton that's available, which is the hydrogen in the water group.

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Instructor: It's going to come and grab the hydrogen which causes the bond to break and the formation of OH group plus a geminal diol. Even though both the mechanisms are slightly different it press the same final product and the almost the same mechanisms. Only difference is when there's a nucleophile attacking, it starts with a nucleophilic attack and then protonation.

00:04:35:01 - 00:04:52:95

Instructor: If it's electrophile attacking, it starts with protonation, followed by a nucleophilic attack. In summary, if we are given a question like this, like in a midterm or final, we'll look at is either our catalyst, a nucleophile or electrophile. If it's a nucleophile we follow the reaction.

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Instructor: Follow the basic reaction. If it's an electrophile, we follow the acidic reaction. So, let's look at this question.

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Instructor: If I was given question like this in the exam, the first thing I will look at... I, first thing,

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Instructor: I would look at look at if it's a nucleophilic attack or electrophilic attack. Since hydrogen doesn't have any electrons, it's a good electrophile. We know this attack is going to be electrophilic.

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Instructor: The first step would be always protonation. The propylene oxygen is going to attack the hydrogen, forming the intermediate with a formal charge. Since this oxygen has a formal charge, it's going to pull the electron density towards itself, making the carbon more electrophilic, like the previous example.

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Instructor: The carbon is going to be more reactive or more susceptible for a nucleophilic attack. So, methanol in the corner right here the oxygen has a lone pair, so it can attack the carbon and... break the carbon oxygen double bond,

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Instructor: which releases the formal charge. This causes a tetrahedral intermediate to be formed, which has SP³ hybridization. This oxygen is trying to get rid of this charge.

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Instructor: The only way for this oxygen to do that is by deprotonate itself, releasing a hydrogen and having no charge at all. The hydrogens going to be kicked out and it's going to form the H⁺ ion that was originally used up in the reaction. If we compare this compound, that's going to be form to a geminal diol, you would see that it has one alcohol group and a CO and oxygen methyl group.

00:07:02:47 - 00:07:19:61

Instructor: This compound that's formed is known as a hemiacetal. It's known as hemiacetal because it contains one alcohol group instead of two on the same carbon. You can figure this out by looking at the solvent we used in this reaction.

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Instructor: Since we use methanol, which can only deprotonate and give oxygen methyl and not an OH group, it's only going to form this compound and not a geminal diol. Now let's take recently formed hemiacetal and react it again in one equivalence to form another compound. As always, the first step would be protonation.

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Instructor: Since it's electrophile as our catalyst. The alcohol group is going to protonate itself and turn into water. Since we know that water is a good leaving group, it's going to leave the molecule.

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Instructor: And form a carbocation. The second step as a previous reaction was nucleophilic attack. Acidic methanol is going to attack the electropositive.

00:08:25:25 - 00:08:45:40

Instructor: It's going to attack the carbocation, forming the intermediate again. From the intermediate. For this intermediate to be to remove the charge, it's going to have to always deprotonate itself, releasing the hydrogen and reforming the catalyst.

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Instructor: It's going to release the hydrogen. As a result, it's going to form a compound which has two...two oxygen

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Instructor: methyl groups attached to the same carbon. This compound is going to be known as acetal. The reason it's going to be known as acetal, not a hemiacetal, hemiacetal looks like a halfway completed acetal as it contains only one oxygen methyl group and alcohol group, whereas acetal contains two oxygen methyl groups in it.

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Instructor: This compound that we form, it's going to be known as an acetal. The reason why it's going to be known as acetal compared to hemiacetal, and acetal is more like a complete version of the reaction. Whereas hemiacetal, hemi means half complete.

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Instructor: As you can see in the hemiacetal, it contains an OH group or O-CH₃ group. Whereas an acetal contains two O-CH₃ groups. This molecule is going to be more sterically surrounded compared to hemiacetal. In summary, carbon compounds that react with alcohols in acidic conditions.

00:10:06:32 - 00:10:27:73

Instructor: If there's one equivalence will form a hemiacetal. If the compound has, for example, excess written in it, it's going to form acetal compound. So, if I start a question like this, I will always look at the reagent to see if it's in one equivalence or excess.

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Instructor: If it's not given, if it's one equivalence or excess, I will assume that it happens in one equivalence, it'll be much more easier. If you take another ketone compound, a random ketone, and if you see these reagents in an exam, how would you do a question like this? The first thing I would do is look at the... look at the catalyst.

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Instructor: If it's a nucleophile or electrophile. Since it's electrophile again, I'm going to react, I'm going to protonate oxygen first. It's going to form the charge intermediate that we see previously.

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Instructor: The next step would be a nucleophilic attack. That attack is always going to break the Pi bond and remove the charge. This attack it's going to be done by nitrogen.

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Instructor: The nitrogen is going to attack the partially positive carbonyl in the carbon group, forming the intermediate again. And the nitrogen is going to get the positive charge, the formal positive charge. Normally, we would remove no...

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Instructor: in order to remove...like

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Instructor: for the nitrogen to get rid of its formal charge, it will have to deprotonate itself and remove hydrogen. The nitrogen is going to remove hydrogen.... Simultaneously,

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Instructor: the oxygen is going to take the same hydrogen and become water and leave. This causes the carbonyl carbon to become a carbocation again. The nitrogen is now going to use its lone pair to form a double bond with carbon. When it does that, it's going to regain its former charge again.

00:12:43:08 - 00:13:06:40

Instructor: So, in order for nitrogen to remove charge again, it's going to have to again deprotonate itself releasing hydrogen reforming the catalyst. So, this compound that's form right now, it's known as amine. It's formed when a carbonyl carbon, let's say a ketone react to the primary amine... primary amine in acidic conditions.

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Instructor: So, this compound that forms right now, it's known as amine. So like all the previous examples, questions we have done before, it always starts identifying if the attacker is a nucleophile electrophile. If it's electrophile, we protonate, then we look at the charges and how they're going to travel if you can remove the charges but deprotonation, we had to gain charge.

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Instructor: If it's a negative charge, it's negative charge oxygen, we gain them by protonation. This makes sense because it's always dependent on the type of solution the reaction takes place and the type of reagents they use. For this reaction, we are using acidic conditions and you see nucleophile.

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Instructor: It's always start with protonation, then nucleophile. Which is similar to geminal diols, hemiacetals, acetals, and so. If you know the mechanism for one of the steps, one of the reaction... one of the reactions,

00:14:06:03 - 00:14:26:73

Instructor: you can use the same reaction, just change the compounds and you'll get the same mechanism for everything. This is another type of question that could appear in a midterm or final. As we seen earlier, we are going to notice if the catalyst is an electrophile or a nucleophile like always.

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Instructor: Since it's electrophile, you know the first step would be protonation. However, we will look at the secondary compound we're being given. It looks similar to the previous amine, but if you look closely, you see it has only one hydrogen group.

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Instructor: This makes it a secondary amine. Since it's a secondary amine, would that affect how the mechanism transfers or would it be the same? Let's take a look at that.

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Instructor: As the first step is already done, the second step would be a nucleophilic attack. The secondary amide is going to attack the same way as the primary as how the primary amine attacked. It's going to attack the partially positive carbocation... carbonyl group, sorry.

00:15:21:68 - 00:15:52:33

Instructor: That causes the Pi bond to break and the oxygen to lose its charge. As we've done in previous questions. Only way for nitrogen, the secondary nitrogen in their mind to lose its positive charge is by deprotonation.

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Instructor: It's going to release the hydrogen become stable. As it releases the hydrogen, a proton transfer would occur like previously and oxygen and the alcohol group is going to take the hydrogen and then fall off, become water and fall off. As the alcohol molecule takes a hydrogen and becomes water and falls off, it's going to create carbocation be formed.

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Instructor: Since the carbocation forming, and nitrogen has a lone pair, it's going to transfer the lone pair to the bond forming and causing a double bond to form. Unlike last

time, this nitrogen can really remove its charge as it doesn't have any hydrogens to remove and it can't remove group. In order in order to remove the charge from the nitrogen, we're going to look at the carbons that are closely connected to this carbon atom.

00:17:01:67 - 00:17:23:82

Instructor: This carbon here, this carbon. Both these carbon have alpha hydrogens in them. So, depending on which depending on your most substitute side, we are going to remove we're going to do proton transfer by removing the hydrogen and forming a double bond between the carbonyl carbon..

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Instructor: carbonyl carbon and removing the double bond between carbon and nitrogen. It'll look like this. The final compound is a lot different than the previous amine, as we don't have a double bond between the nitrogen and carbon... carbonyl carbon.

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Instructor: However, we do have a double bond between two carbons. This reaction looks more like the final product looks more like alkene, which has an amine substitute group with it. This compound will be known as Enamines. Enamines are formed when the carbonyl compound

00:18:08:45 - 00:18:42:45

Instructor: reacts with the secondary amine group in acidic conditions to form this, whereas an amine forms when a primary amine group reacts with carbonyl compound in the same conditions. In summary, all the reactions between geminal diols, acetals, and amines follow the same mechanical principle. It's going to protonate, a nucleophilic attack, wearing of charges, and finally, reformation catalyst H^+ .

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Instructor: So, another important reaction that carbonyl compounds can undergo it's known as Wolff-Kishner reduction, where we take a ketone and then we reduce it to alkene. So, the general reaction is going to be as follows. Okay. So, let's take acetone, for example.

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Instructor: We are going to react acetone with a hydrazine known as...

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Instructor: This compound is known as a hydrazine. This reaction is also going to happen in acidic conditions, and it's going to look like this reaction is going to have the same mechanism like an amine, so you can try it yourself. The final compound that's formed from that reaction is going to be known as a hydrazone which is an amine derivative.

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Instructor: This is the first part of this reaction. The second part would happen would be a serious set of elimination reactions where I would go in detail show you mechanisms. The

second part of this reaction would be an elimination reaction where we obtain an alkane group.

00:20:06:00 - 00:20:38:95

Instructor: We're going to take the formed hydrazone and react it with a strong base at high temperature. The first step I will look at if it's a nucleophile or electrophile, since sodium is a strong base, it's going to deprotonate giving you Na^+OH^- . Since OH is a nucleophile it's going to deprotonate one of the hydrogens in the nitrogen group.

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Instructor: This results...result in

00:20:41:89 - 00:20:45:71

Instructor: the nitrogen group having....This

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Instructor: results in the nitrogen group having a negative charge due to having an extra lone pair. Normal sodium hydroxide is an aqueous solution, so I forgot to add the water into this. Let's just put up here.

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Instructor: Water. Since nitrogen is now negative charge, it's going to add the lone pair to the nitrogen...

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Instructor: and it's going to add the lone pair to the nitrogen bond forming a double bond. As this double bond forms, then the nitrogen is going to give the lone pair carbon, making it an ion, and making it a carbonation. This carbonation is going to strip and hydrogen from the water, which is going to be first hydrogen that's going to be added to this reaction.

00:21:39:12 - 00:21:59:01

Instructor: As a carbon on it, strips the hydrogen away from the water, it's going to reform the base, the hydroxide ion. It's going to reform the hydroxide ion. This is the first hydrogen that's added to this reaction.

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Instructor: Since now we have the base formed here again, it is going...

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Instructor: Step two, what we did right now, it's going to happen again. Since we have the hydroxide ion, we can redo step two by stripping the hydrogen away, forming a negative charge here, then me going to triple bond. And the car and it's going to reform carbon ion again.

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Instructor: It's going to look like this. Water is going to reform again...

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Instructor: Water is going to reform again and the nitrogen dioxide is going to form, which it's going to release as gas. Plus, negative carbonation, carbon. As water is reformed again, the same step that happened where the carbon strips the water again as the nitrogen carbon bond breaks and the nitrogen gives its lone pair forming a triple bond.

00:23:07:97 - 00:23:10:85

Instructor: Nitrogen is going to...and forms

00:23:10:85 - 00:23:13:51

Instructor: a really strong...stable bond

00:23:14:18 - 00:23:30:86

Instructor: which has high bond enthalpy, which is stable. It's going to leave as a good leaving group and be released as a gas. And finally, the secondary hydrogen is going to be added the same way the primary one.

00:23:30:86 - 00:23:39:78

Instructor: The first hydrogen was added. The carbon is going to strip one of the remaining...strip one of

00:23:39:78 - 00:23:51:10

Instructor: the hydrogens from the water molecule, regain...reforming and forming and alkane as a result.

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Instructor: Alkane as a result. so, we could use the Wolff-Kishner...

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Instructor: In summary, we could use the Wolff-Kishner reduction in order to remove the C double bond O, and obtain an alkane... obtain alkane.

00:24:08:05 - 00:24:24:47

Instructor: We could use a Wolff-Kishner reduction to reduce a carbonyl group into an alkene compound. The final reaction we'll look at is the Baeyer-Villiger oxidation reaction. In the Baeyer-Villiger oxidation reaction, we are going to react a ketone.

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Instructor: We're going to oxidize a ketone to...so

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Instructor: Let's take a random ketone, a random ketone, for example. Ketone. They're going to react this ketone with the pre acid.

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Instructor: Three....

00:24:55:15 - 00:25:08:89

Instructor: We would react this ketone with a pre acid. Pre acids are compounds which contain an oxygen, which is bonded to oxygen, that's one to carbon, which contains a double bond. So, compounds such as MCPBA, which is a pre acid.

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Instructor: So, for this reaction, the easiest way that you could do it is find the most substituent side of your ketone or carbonyl compound. For this question, it is the most left side carbon. I'm going to circle most left side carbon.

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Instructor: Since you're making an ester, Esters consider C-level 10, carbon that's bonded to another oxygen bonded to the carbon...

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Instructor: Bonded to another carbon. So, we're going to do is they're going to break the bond between this, grab an oxygen and insert it straight into the bond. So, the final product from this oxygen reaction should look like.

00:26:03:67 - 00:26:10:85

Instructor: This is what's going to be form, which is ester. One of the... To make this question much easier,

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Instructor: you can do is label the carbons one, two, one, two, three, four, five, count your carbons. And then, in the product side, you can count the number. If the carbons don't match up, then there's something wrong with the product.

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Instructor: That's one, two, three, four, five, six, six carbons here, one, two, three, four, five, six, six carbons there. So, can this reaction work with rings? That's one of the things we're going to look at next.

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Instructor: So, let's just take... Let's take cyclohexanol,

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Instructor: hexanol, which is a six-member ring. So, it has six carbons in it right now. So, the product is going to also have six carbons, as we know, as we see in the above example.

00:27:02:27 - 00:27:11:69

Instructor: So, let's just write randomly here. We are going to react. We're going to take the same pre acid and just react.

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Instructor: Like previously, they're going to look at the most substituted side. Since this molecule is symmetrical, it has the same opportunity to go to the left or to the right. In this

case, it doesn't really matter where the oxygen is going to be attached because it's symmetrical.

00:27:30:71 - 00:27:49:14

Instructor: Let's take the right for this example. You're going to break the bond in the right side, and we are going to insert oxygen right into this. We're going to insert so you're going to insert this oxygen right into this.

00:27:49:14 - 00:28:01:16

Instructor: You need six carbons. So, it's going to look like some. It's first carbons here, second, oxygen, third, fourth, fifth, sixth.

00:28:01:16 - 00:28:26:91

Instructor: If you connect them, it's going to look like a seven-member ring. Even though this looks like a seven-member ring it contains the same number of carbons as the starting compound. This reaction would just form an ester without increasing the number of carbons, always count your carbons, look at the most substituent side, and then this reaction should be much easier.

00:28:26:91 - 00:28:44:93

Instructor: If we had this compound, but it's more branched, more substituted in one side, how would you solve it? Compound that you can try at home is this. It's going to follow the same reactions, the same steps we need, just practice.