Introductory Organic Chemistry – II
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Enols and Enolates: Molecular Orbital Picture

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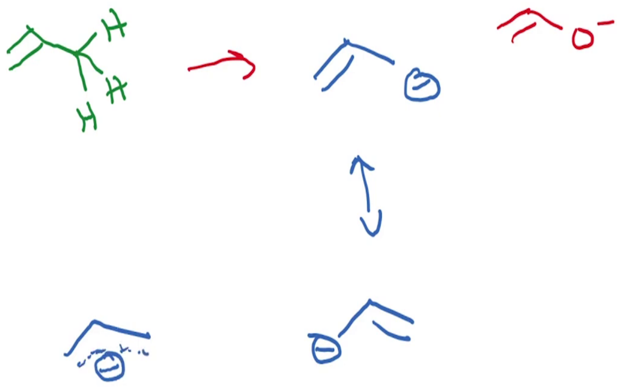

So, now let us look at the molecular orbital picture of the enolate. And before we go there, let me just draw out a simpler system that we can try and understand first before we get there. So just to remind you, this is the enolate that we are looking at. And so parallel structure that we are all familiar with is the allyl group. So, if I start with this kind of a system, let us say, basically, this is an olefin attached to a methyl group.

And if you pull out H^+ from this, then you end up with a system such as this. This is the allyl anion. Now, we want to look at the molecular orbital picture of this. And before we do that, let us just draw out its resonance form, which is as follows. So, you have a negative ion on the terminal carbons. So, therefore, this is represented by us many times as a delocalized negative charge on these three carbons.

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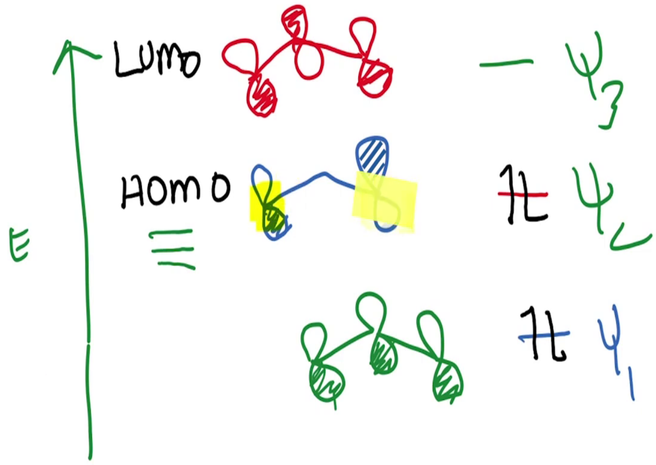

Now, let us look at the molecular orbital picture. So, the molecular orbital picture is as follows. So, you have energy over here. And so, basically, you have three p orbitals, and if these three p orbitals combined, in a favourable manner, so you get the lowest energy picture with the orbital, which is this, so, they are all of the same sign. I am going to call this Ψ_1 and now Ψ_2 would be the orbital wherein you have mixing going on, but there is a node, so, the way it is drawn is the following and so, this is the picture how it's shown.

And now, the third orbital, when you mix it, the third orbital that is going to be produced is the orbital where the signs are opposite to one another, which produces an unfavourable situation. So, that would be Ψ_3. And now, in the case of the allyl anion, you have two electrons from the pi bond and two electrons from the negative charge. So, the way we would draw it is this, so, these two are filled.

So, please pay particular attention to this, because this orbital is the HOMO, the Highest Occupied Molecular Orbital and this is the LUMO which is the Lowest Unoccupied Molecular Orbital. So, as we discussed earlier, in terms of reactions when a negatively charged species reacts, the most important orbital that we would like to consider is the highest occupied molecular orbital and when a functional group is acting as electron acceptor, then orbital that we need to consider is the LUMO, the lowest unoccupied molecular orbital.

So, therefore, the electron density according to this map, according to this molecular orbital picture suggests that the maximum electron density is at the terminal carbons as shown here. Now, there is some experimental evidence that supports this claim.

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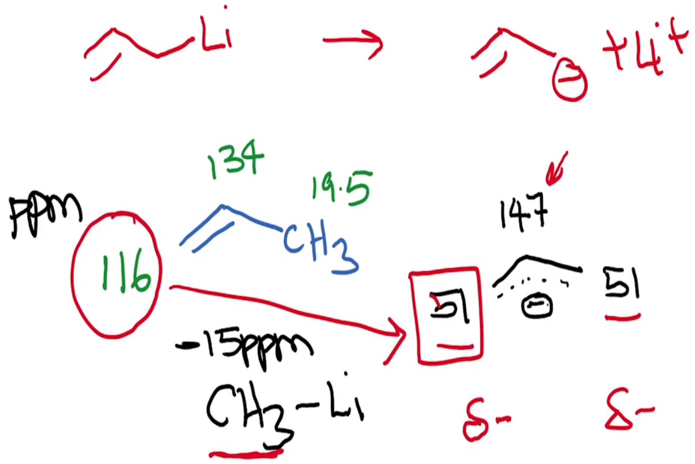

So, for example, allyl lithium is a commonly available reagent and I know when we record the NMR spectrum of this, this is going to dissociate to give this anion and Li^+ and so if we record Carbon-13 NMR spectrum, then what we see is very interesting picture. So, if I start with propane, then I would get the Carbon-13 NMR spectrum, we would get signals such as this where this is 19.5 ppm, this is 134 ppm and this is 116 ppm.

So, this is what you would get if you just record propene's NMR spectrum and if we take the NMR spectrum of methyl lithium, then we see a peak at -15 ppm. So, therefore, all of these values are in ppm. So, therefore, this methyl lithium pushes the value or the chemical shift value all the way too much below 0. And so, when we record the NMR spectrum of this allyl lithium, then what we get is we get only two signals, we would expect, essentially three signals, but we see only two signals, one is at 147 ppm, and the other one is at 51 ppm.

So, which is assigned to this delocalized anion as shown here. And the interesting thing here is that it supports our molecular orbital picture in a couple of ways. One is that because you have a resonating form over here, that is between this, the negative charge spends time on this carbon as well as this carbon, and therefore, it is going to be delocalized, you see only two signals here, as opposed to what you would expect would be three signals if it is spending time if the negative charges localized only to one of the carbons.

And the second thing here is that once the carbon has a negative charge, you see that the value of the chemical shift goes down substantially. So, for a normal olefin, what we would expect is the value between 120 and 130. But we get a value of about 51. So, this substantial jump in the chemical shift suggests that this carbon has a strong negative charge, of course, it does not have a full negative charge, it would have a strong partial negative charge. So, I will repeat this concept once again. There are two points about this experiment.

The first one is that the two ends of the carbon are the same because you get only two signals when you record the NMR spectrum of allyl lithium. And this tells you that there are only two carbons, two distinct types of carbons. And so, one is this peak at 147. And the other one is 51.

Point number two, most of the negative charge is localized in the two corners, so that is two terminal carbons, which would be 51 and 51 ppm. And this tells us that the most reactive center in this anion is the terminal Carbon. So, with this background, let us now look at the enolate, the picture of an enolate.

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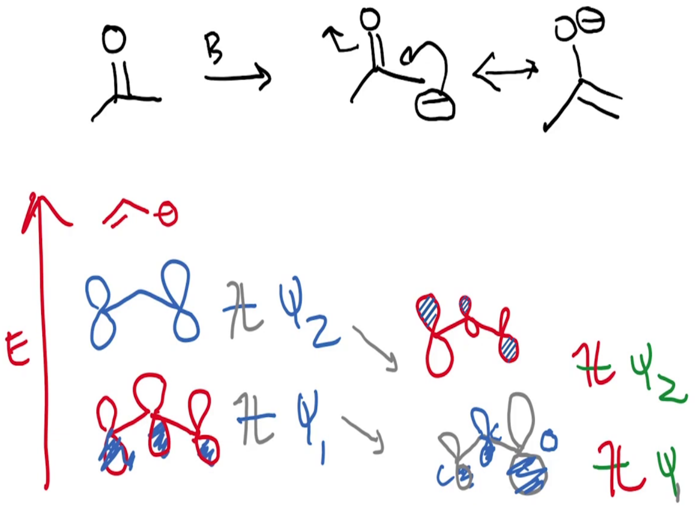

So, just to recap, an enolate is generated when you react base for example, with the ketone, and so this is the carbanion, and this is going to delocalize or is going to push its negative charge into the oxygen, and you are going to get a enolate anion. So, now if I have to construct a molecular orbital picture for this, then what I would need to do is let me juxtapose these two pictures, so that it is easy for us to understand. So, this is the energy.

So, for the Allyl anion the way we understand it, is that now we are only considering the LUMO So, there are three p orbitals which are mixed, and these are shaded, and this is your Ψ_1. And the next one. Is this where you have a node. I think all of you know what a node is. So, this is Ψ_1 and Ψ_2. So, now, when these electrons are filled, you get a system like this, where you have this allyl anion.

Now, if I have to look at the same picture, for the enolate, what ends up happening is that because oxygen is more electronegative, this brings down the energy. So, when compared to Allyl anion, so the Ψ_2 and Ψ_1 would be lower in energy compared to the allyl system. So, this is because of the, we have already looked at it earlier, when you have an electronegative atom bound, then it is going to lower the energy. Now, being an electronegative atom, we have also seen previously that this distorts the orbital picture substantially.

And so, the picture is going to look something like this where you have a much larger lobe for oxygen, and a smaller lobe for carbon, you need to look at your textbook for the more accurate picture, but I am just drawing this so that you guys understand. So, this is the oxygen and this is the carbon. So, this would be my Ψ_1. And now when I come to Ψ_2, which is the next highest orbital, we have a larger lobe in the carbon and then a much smaller lobe in oxygen, and so, therefore, the orbital over here is much smaller compared to the oxygen for Ψ_1.

So, these are the two molecular orbital pictures. Now, so therefore there are two important takeaway points, number one point is the oxygen is more electronegative. So, therefore, it brings down the energy. So, if you compare the Ψ_2 of the allyl anion versus the Ψ_2 of the enolate, the energy of the enolate is substantially lower. The second one is that the electron distribution is happening across all three atoms. And in the Ψ_1, you have a larger lobe for oxygen, and in Ψ_2, you have a larger lobe for carbon.

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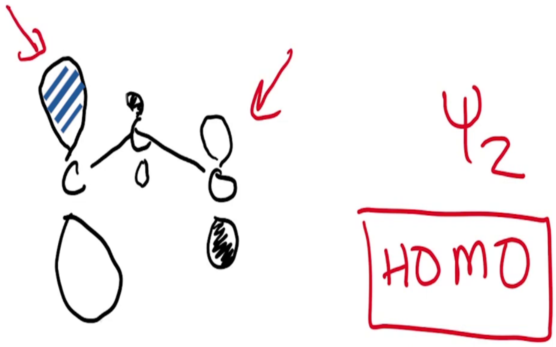

Now, this, I am going to redraw in the next page because I want to discuss this a little bit. So let me look at the Ψ_2 because that is an important orbital for us to look at. So, when I draw this out, again, I am just drawing it out again, for us to understand this. There is a very small component to the center carbon, but this is my oxygen and these are the two carbons. And the way we have shaded it is like this.

So, this is my Ψ_2. And as you recall, this would be the highest occupied molecular orbital. And therefore, this plays an important role when we are looking at how this is going to react. Alright. So now, in terms of the reactive orbitals, we found that the allyl anions, both the carbons are equally reactive because the size of the lobe on both the carbons was identical.

But what we also figured out was that the center carbon is not going to react because there was no orbital there for it to react in terms of an electron donor.

So, in an enolate, you see that the size of this lobe, let me just redraw this so that to make it a little clearer, so you have two carbons and one oxygen, but just to be clear, this is the carbon, this is the carbon and this is the oxygen. And so, the size of the lobe here is substantially larger on the carbon, I am just drawing it very large, just to make the point.

And there is a very small component on this carbon and this carbon the terminal carbon is going to play an important role in determining how reactions happen. So, now, what we can suggest is that the two reactive centres on this enolate are these two that is this carbon and this carbon, and the way in which these reactions occur is going to be different when compared to an Allyl anion.

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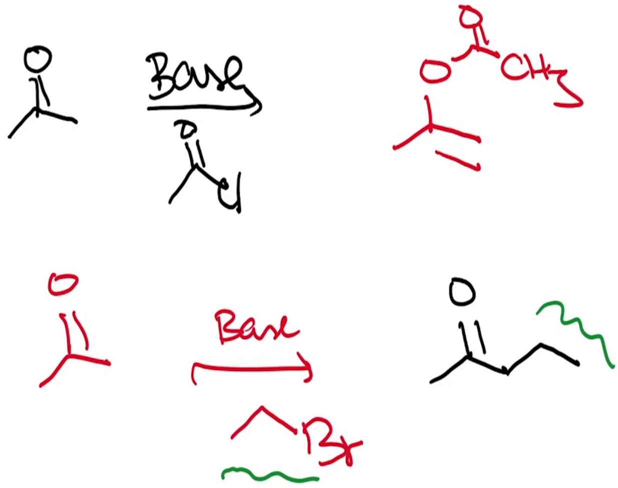

Now, when we do an experiment, we will find out, if we can reason this out, when we do an experiment, for example, when I take and acetone and react it with some base and add an acyl chloride, the product that I get is $CH_3(OC{=}OCH_3)C{=}CH_2$, the product is the one that gives you the O acetylated product.

So, this is the product that I get, whereas when we react base, and I react it with let us say, ethyl bromide the product that we obtained is this, So, where this ethyl group has come from this ethyl bromide.

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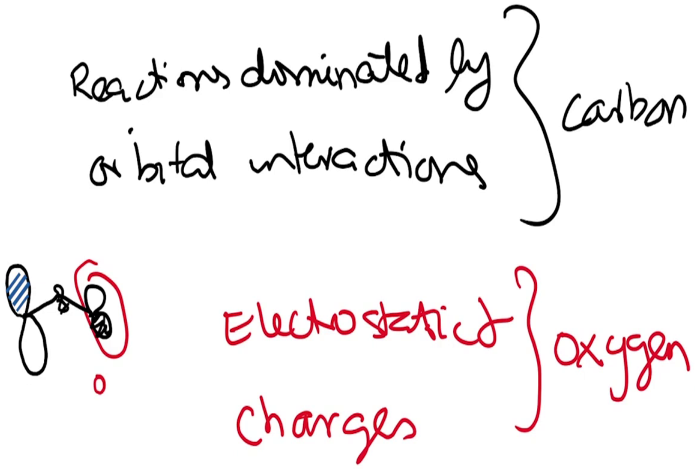

Now, the way we want to understand this difference in reactivity is through the molecular orbital picture. So, the reactions that are dominated by orbital interactions, these are occurring at the carbon. And this is somewhat reasonable because we realized that in the enolate, the largest orbital of the HOMO was located at the carbon. So just to recap, so this was the largest orbital, and then there was a smaller orbital which is small orbital here.

So, this is the way in which we will draw this picture. And whereas, if you see the oxygen which is over here, the oxygen reacts when there is a reaction that is dominated by charges. So, when the O^- has a very significant amount of, that is the oxygen being the more electronegative atom has a stronger charge component on it and therefore, the reactions which are dominated by charges and electrostatic interactions.

So, electrostatic and charges these are reacting at the oxygen. So, therefore, substantial difference or an important difference between the enolate and the allyl anion is that the allyl anion is very symmetric and both the ends are equal and so, therefore, there is no difference in which end reacts whereas, in the enolate, there are going to be differences that are going to come in and one important difference is that the oxygen being electronegative has the greater charge on it.

And so, therefore, reactions which are dominated by charges by electrostatics occur at the oxygen. Whereas, reactions which are dominated by orbital interactions, being the HOMO of the enolate has a larger lobe at the carbon, and therefore, this dominates the reactions that occur at the carbon center. Now, we will discuss this in more detail in the coming chapters when we look at how to generate the Enols and Enolates. But right now, it is important for you to recognize that there is a difference between the carbon and oxygen in terms of reactivity.

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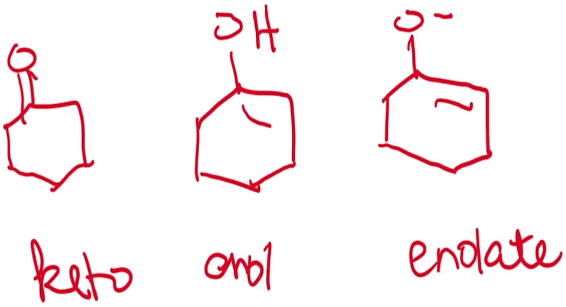

Alright, so now let us summarize the various aspects of enol and enolate chemistry. So, if we start with Cyclohexanone, and for cyclohexanone, we could draw out, this is the keto form, which is just cyclohexanone. And the enol form would be in the following manner. This is the OH and the enolate is this.

So, this is the enolate. This is the enol. And this is the keto. So, these terms I think we should all get quite familiar with. And once these are clear, then I know we do not need to worry too much because the rest of the course we will be coming back to these terms again and again.

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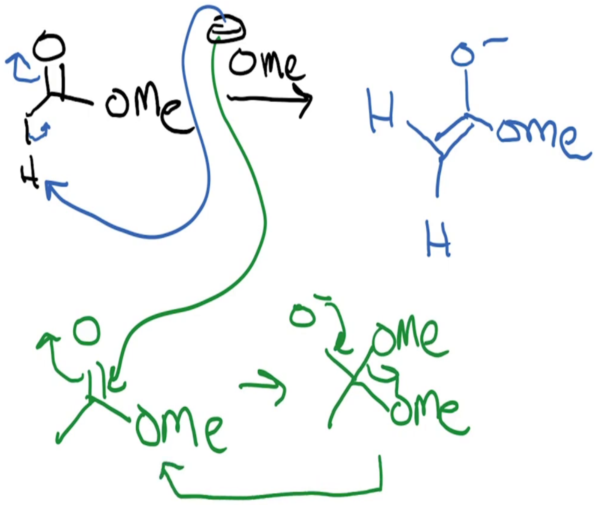

Now, as you know carbonyl compounds there are several varieties of carbonyl compounds. So, one variety of carbonyl compound that we all know is the Ester. So, a typical Ester is shown in the following manner $CH_3C{=}OOMe$, let us say I take a methyl Ester. And now when I add a base to this, $^{-}$OMe, then what can happen is that this hydrogen over here, this negative charge can come and attack here, and it can generate a Enolate.

So, this enolate of a carboxylate anion can be generated under these conditions. And now you can ask me the question, what happens if the methoxide attacks the carbonyl? So, let us consider that option now. So, when OMe, if methoxide attacks here instead, which it can certainly do, then it is going to produce the tetrahedral intermediate that we are quite familiar with. So, O minus, and then there is a CH_3 over here. And now this can come in here and kick out this methoxide and it is going to regenerate the ester. So, using right base for generating the enolate is very important.

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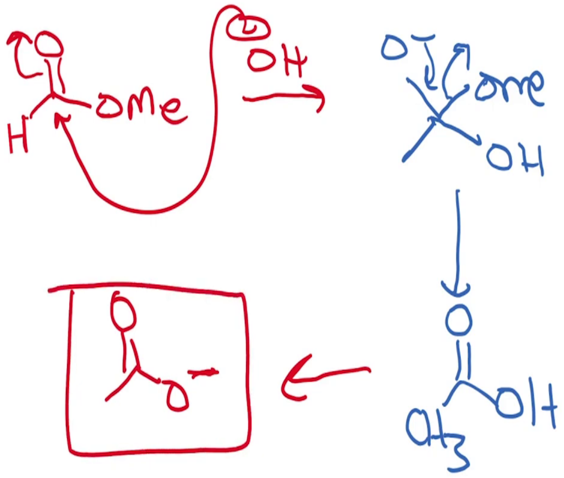

Now, you can also think about the possibility of using hydroxide, which I accidentally drew at the beginning of the slide, the previous slide, but what happens if you use sodium hydroxide instead of methoxide? Then what can happen is you have a competition between two things. One is that it goes here. And the other one is it goes to the alpha position. But let us first consider this it goes here. And then it produces the tetrahedral intermediate. Great, and you have OH.

Now, when it comes back in, it can do two things, it can either kick out methoxide, or it can kick out hydroxide. And if it does kick out the methoxide, then what it is going to produce is it is going to produce a carboxylic acid. And when this carboxylic acid is produced, you all know that in the presence of a base, it is going to very quickly give you the carboxylates which is not going to further react. Now, therefore, this reaction is going to be favoured when you use a nucleophilic base, such as hydroxide ion, and so you are going to get the carboxylate ion.

Now, the second possibility of picking up alpha hydrogen can happen, but once it picks up the alpha hydrogen and produces the enolate, that is going to go back and produce this again and this reaction is going to dominate because of the formation of the carboxylate ion.

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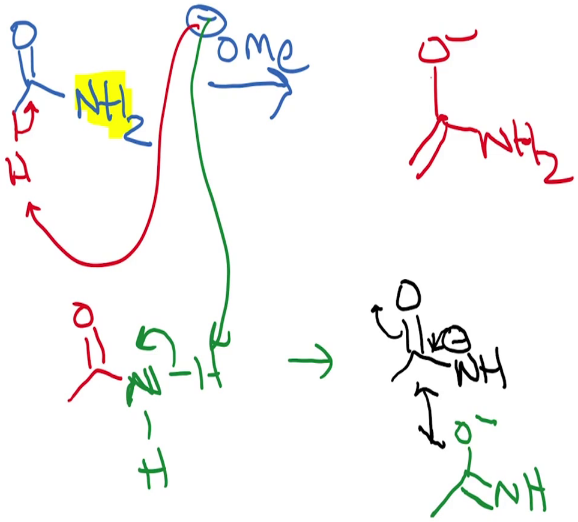

Now, when we look at the next case, which would be, the formation of amides or formation of enolates from amides, so let us consider that. So, you have CH_3 C=O NH_2, and now when I expose this to a base, let us say let us use sodium methoxide again as the base, $^{-}$OMe. So, now when I expose this to this base, now the methoxide can again do a couple of things, this is indeed a proton that can be picked up and you can generate the enolate as we are quite familiar with.

And however, there is a problem here, the problem is that this NH_2 Actually, this hydrogen is quite acidic, you might have studied about this in the previous semester. And so, what happens is instead of producing this kind of an enolate, what may end up happening is that you have NHH and this methoxide now attacks here and it produces a fairly stable amide anion.

So, you have a $CH_3C=ONH^-$. These amide anions, one of the reasons why this is stable is, it sort of, it can de-localize and it can produce the resonance form as shown here, which is $CH_3O^-C=NH$. So, because of this possibility, I mean, or rather, we understand the stability of this amide ion by invoking this concept of as shown here. So, amides are not very conducive to producing enolates, or at least amide with NH_2 on it, they are not conducive to producing an enolate because of the formation of this kind of anion.

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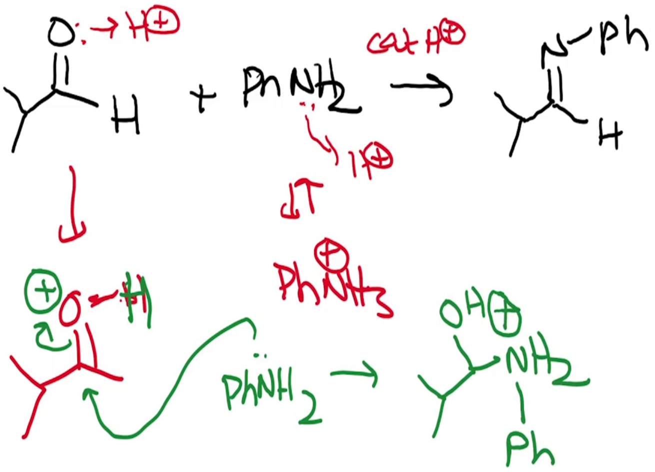

Now, the last thing that we need to look at, or one of the last things that we need to look at is what happens when you react a ketone with an amine, so again, this is something that many of you are familiar with, but I will quickly revisit it. So, when I take aldehyde and react this with, let us say, Aniline, Ph NH_2.

And now, what we end up getting is, an imine, which I am hoping that all of you are quite familiar with. But let me just go through a little bit of background here. So, when you add these two reagents together, and you add a catalytic amount of H^+, so what you can suggest is that this NH_2 is clearly the better base so it is going to pick up a proton and it will be in equilibrium with Ph NH_3^+.

But since there is a small amount of acid, you can imagine that once in a while, this picks up this proton from Ph NH_3^+ perhaps, and it gets protonated. So, once it gets protonated you are going to produce $(CH_3)_2CHCH{=}O^+H$, so this OH plus is quite a nicely activated carbonyl substrate. And now your amine, just in a fairly large concentration compared to the proton can attack and you will expect to get this is kind of an intermediate where you have $(CH_3)_2CHCH(OH)NH_2^+$ Ph, and keep in mind that this positive charge is still here. So, now let me draw this intermediate up in the next slide.

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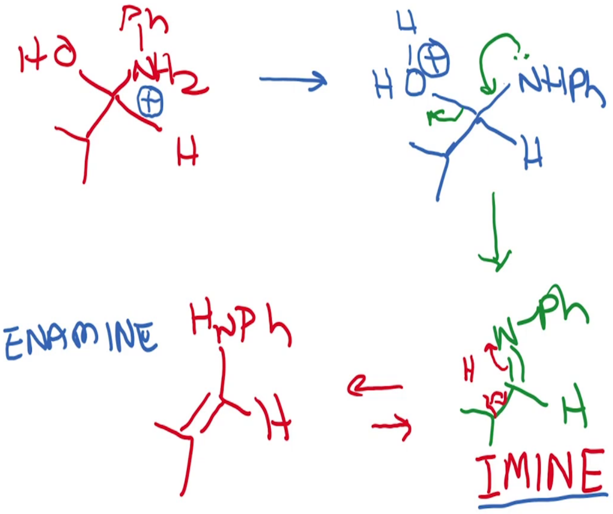

So, NH_2 Ph OH and we have a hydrogen here and we have an isopropanol group here. So, and this positive charge remains over here. Now, what can happen is that you can have a transfer of this proton from amine cation to the hydroxyl group and you will end up getting this protonated water species. So, you have $(CH_3)_2CHCH(OH_2^+)NHPh$

Now, know what can happen is that this lone pair of nitrogen can now come in over here and kick out water as you know water is an excellent leaving group. And so, if it does this, then you get your imine. So, this is what happens when you have a primary amine. So, this is called the IMINE. So, it is not I MINE, it is IMINE and this IMINE is a very important intermediate that we will look at later.

But just like a carbonyl compound, this imine has alpha hydrogen. So, we have been discussing about how enolization, etcetera can happen. So, it is entirely possible that this sort of undergoes some sort of tautomerism and it can produce $(CH_3)_2C{=}CHNHPh$. And it can produce this kind of intermediate, so this intermediate is called the Enamine.

So, just to revise this concept, so you have the formation of an Imine, which is shown here, and then you have the formation of an enamine. Again, you can go back to your textbook, this is in the formation and reactions of enols and enolates, and you can go back and look at it. So, this is what happens when we start with a primary amine. But now what happens when we use a secondary amine.

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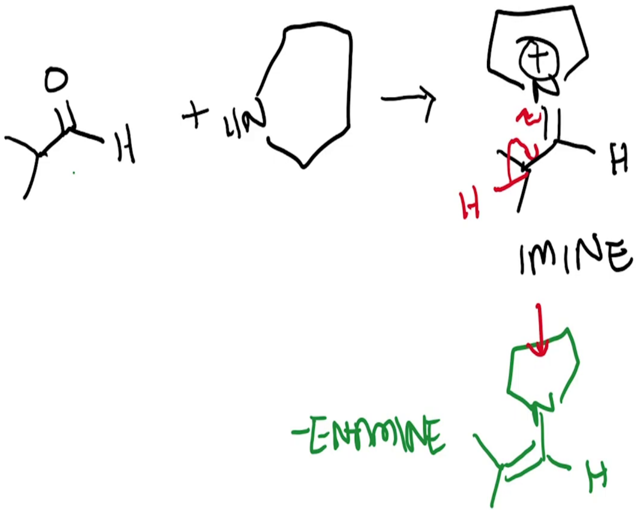

Let us look at that, then that should conclude the lecture on this topic. So, what happens let us say the example that we can take is this. So, this is the pyrrolidine. And so, when Pyrrolidine, basically reacts with this aldehyde, what the product that you get is going to be, if I extend the same logic of the production of the Imine, then you are going to get an Imine such as this.

But the interesting thing here is that you have a proton that is going to be enolizable. And so, if you again push electrons, you are going to get the formation of fairly stable Enamine. So essentially, what happens is that when you start with the ketone, you get an Enol, you get an enolate, when you start with an ester, you can get an enolate that is derived, provided you use the right kind of base. If you use hydroxide, for example, you are not going to get the enolate but you end up getting a carboxylate.

And, amides are a case where you do not have the formation of the corresponding enolate, but instead, you get the amide anion, but you can generate Imines and Enamines by using carbonyl compound, and the corresponding primary or secondary amine. And when you use a primary amine, you end up getting a mixture of both the Imine and Enamine.

And generally speaking, the Imines in this case are more stable. But when you use a secondary amine, such as pyrrolidine, the major product that you would end up getting is the Enamine. So, with this background, I think we can now move on to some of the reactions of Enols and Enolates.