Mechanisms in Organic Chemistry
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Lecture-03
Types of Polar Reactions

So welcome to third lecture. Before we start just a recap of what we did in the earlier lecture.

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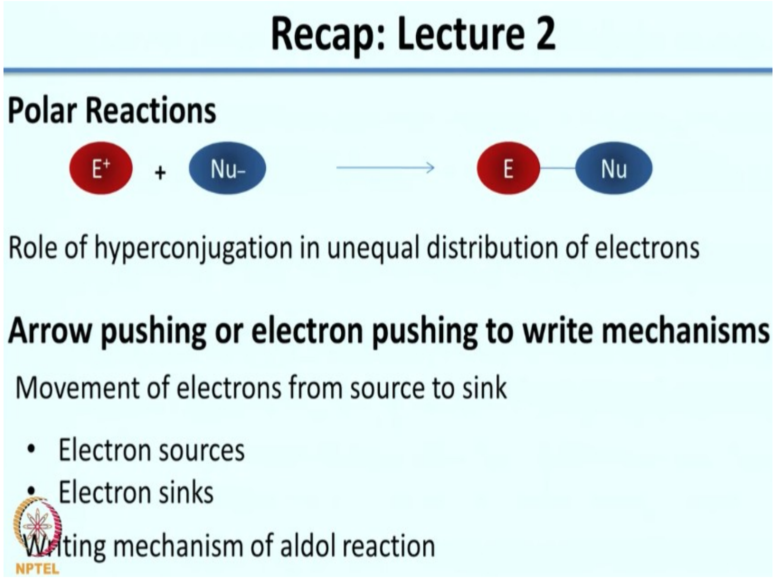

Recap: Lecture 2

Polar Reactions

Role of hyperconjugation in unequal distribution of electrons

Arrow pushing or electron pushing to write mechanisms

Movement of electrons from source to sink

- Electron sources
- Electron sinks

Writing mechanism of aldol reaction

So, we had first classified organic reactions and in particular we were looking at polar reactions. So, when you think of polar reactions you have an electrophilic center and a nucleophilic center and we had looked at the role of hyperconjugation in the unequal distribution of electrons and in lecture 1 we had looked at the inductive effect and resonance effect. Then we had also looked at actually writing mechanisms by arrow pushing or electron pushing and we had looked at how to move electrons from electron sources to electrons sinks.

And I had given you examples of different types of electron sources and different types of electron sinks and we had stopped by writing the mechanism for the aldol reaction. And before stopping I had asked you to work out two problems, one is the acid catalyzed, aldol reaction and I told you the medium is very important.

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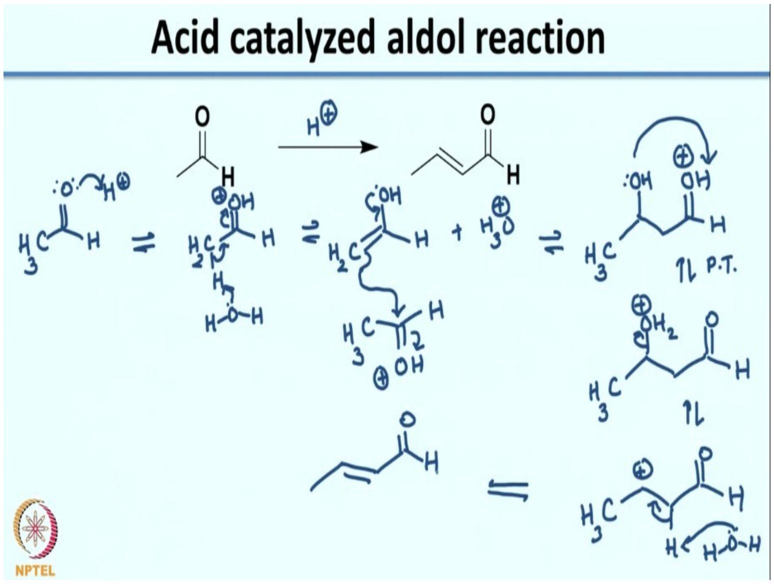

Acid catalyzed aldol reaction

So, we had looked at the aldol reaction which is base-catalyzed. So, now we are going to look at the acid catalyzed aldol reaction. So in the base catalyzed reaction the medium was rich in OH^-, here we are looking at a medium which is rich in H^+. So, obviously, you know what your sink will be in this case it will be H^+, so now let us look at the source, so if I consider again the same molecule.

Now what would be a good electron source here? You can pause your video and think for a minute, if you have not written the mechanism. Alright, so a good source would be these lone pairs on your aldehyde oxygen. So, this lone pair can grab a proton, so what you end up generating would be this protonated species. Now what we would do is I am going to write this methyl as CH_2H.

Because now I have an acidic proton here and this can be grabbed by remember the medium is acidic so you will not have OH^- there, so it would be grabbed by water. So, what I would be generating would be an enol. So as before if you notice the net charge has been balanced here. So, I started with a net positive charge and that has been maintained throughout. Now the next step would be reaction of the enol with another molecule of the aldehyde.

And now since it is in an acidic medium the aldehyde will exist in its protonated form. So, now I have, so what I end up getting, if you systematically push arrows you typically will not make any mistake while writing reaction mechanisms. So, do not try to write too many steps together because that usually leads to a problem when you write reaction mechanisms. So, again you have a net positive charge and the charge is being maintained, the next step would be a proton transfer.

So, you have a source within the same molecule, so it would grab a proton and typically you write this as PT which indicates proton transfer. So, now what I would like you to do is again look from the beginning to the end and maintain and see in every step, what was the source and what was the sinkis. So, now the next step would be, so it would be generation of this carbocation.

Again, as I said the net charge is maintained and then you can think of the water again grabbing a proton to give you the final product. So, again what you see is as you change the reaction medium there is a change in the mechanism Alright? And again I would like to emphasize multiple times that when you have an acidic medium do not try to use OH^- because it will not exist in the medium.

Similarly if you have a basic medium do not try to write H^+ when you write the reaction mechanism. Now let us come to the second problem, now in this problem you could look at multiple sources.

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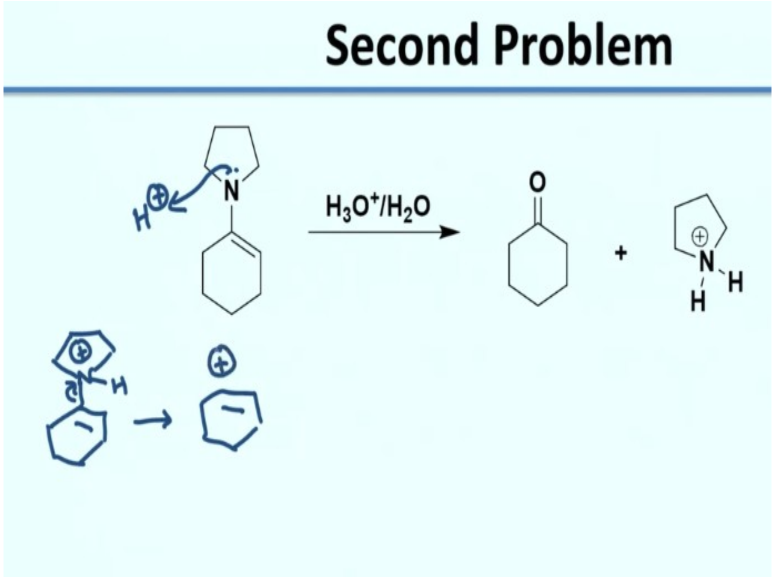

See you have a double bond here which is electron rich which is an excellent source. But some of you might be tempted to directly protonate the nitrogen lone pair here. So, let us see what happens if you directly protonate that. So, if I directly protonate the nitrogen lone pair what I would end up generating would be a species which would look like this. Now what can the molecule do after generating the species.

The only option would be to generate this cation which is highly unstable, so the molecule will not like to do something which makes it so unstable so this will not be a reaction path. So, let us go ahead and erase this because this will not be a good reaction path. Now one thing which I want to tell you when you write mechanisms is do not feel afraid to push arrows and write a possible mechanism just like I did now.

Because even if you make a mistake it is fine you can go back and then write another pathway, but it is very important that you actually write the reaction pathway that you first think of.

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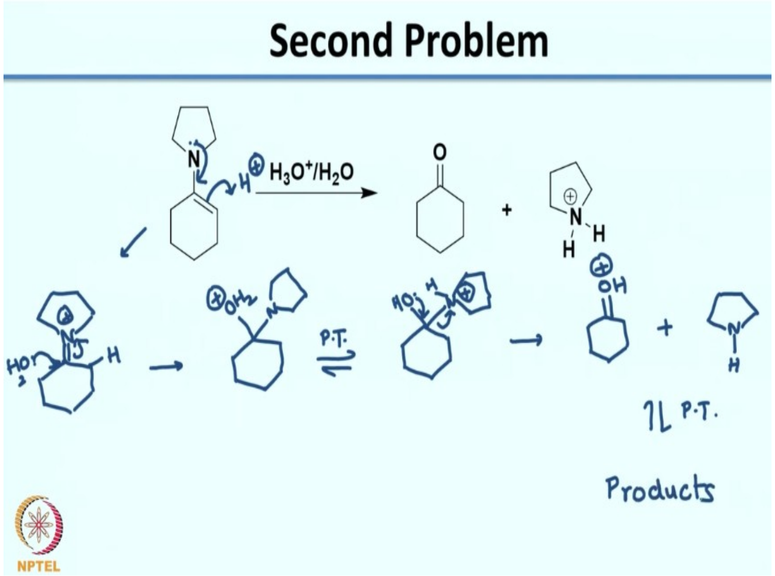

Second Problem

Now let us look at the second case. Again I put the lone pair here. I can think of the lone pair coming here because it is in conjugation with a double bond and then I can think of the double bond grabbing a proton. So, the species that I generate would be, now once I generate the species the next step would be reaction with water. Now let us look at the electrophilic centers or the sinks in this molecule.

So, water can react at this carbon center here and what you would end up generating would be, so again you would be generating this tetrahedral intermediate. Now once you generate this intermediate as I told you in the previous step you can do in the previous aldol mechanism, you can do a proton transfer. So, what you would end up getting, so you can do a proton transfer, so what you end up getting would be always remember to put the charges properly.

Now again once you do the proton transfer these lone pair of electrons can come in and what you end up generating would be. Now again once I have these species I can do a proton transfer to give you the products. So, again, if you write very systematically the reaction mechanism there is very little chance of you falling into any trap or making any kind of mistake. And again as you see in the previous case I have maintained the medium as acidic and also the net charge has been balanced.

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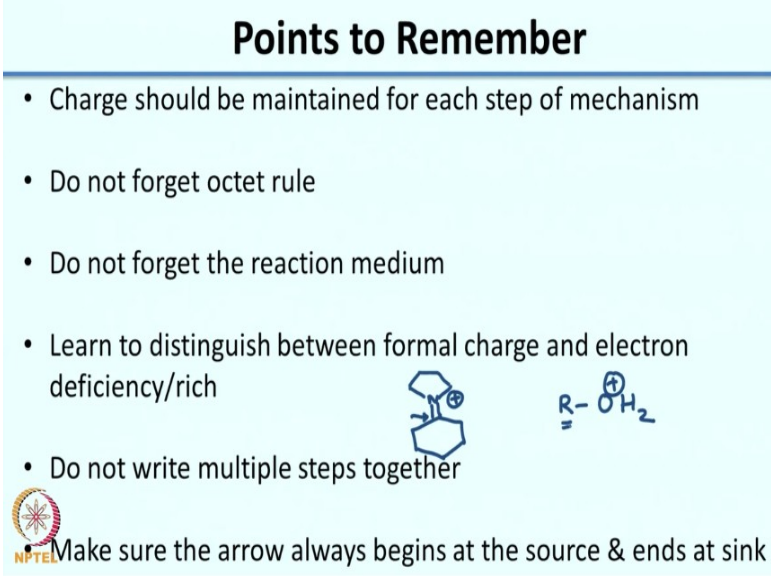

Points to Remember

- Charge should be maintained for each step of mechanism
- Do not forget octet rule
- Do not forget the reaction medium
- Learn to distinguish between formal charge and electron deficiency/rich
- Do not write multiple steps together
- Make sure the arrow always begins at the source & ends at sink

So these are some points that you need to remember when you write reaction mechanism, charge has to be maintained for each step of the mechanism. So, I emphasize this in all the 3 mechanisms that we wrote so far. The other thing is do not forget the octet rule, that is very basic. See, you cannot have like more than the allowed number of bonds at a particular atom. Do not forget the reaction medium.

As I told you acidic medium will not have OH^- and basic medium will not have H^+ and learn to distinguish between formal charge and electron deficiency. So, if you see in the earlier example that we had done, you had, so, in the previous example that we had seen you had a charged species but the electron deficient center was a carbon next to the nitrogen. So, you need to be able to distinguish between formal charge and electron deficiency.

Another example which we had seen earlier is, suppose if you have here again you have a charged species but the electron deficient center is the carbon that is next to the protonated OH. Alright? So, this is something which you have to be very careful when you think of electron sinks, it need not mean a charged species. Also do not write multiple steps together. Why I am saying that is if you try to write multiple steps together there is a greater chance that you tend to make mistakes.

So, be very systematic and write each step independently. And again, the basic rule is always make sure the arrow begins at the source and ends at the sink. Ok? So, this is what we had started off when we were talking about reaction mechanisms. So, let us look at good examples and bad examples of arrow pushing.

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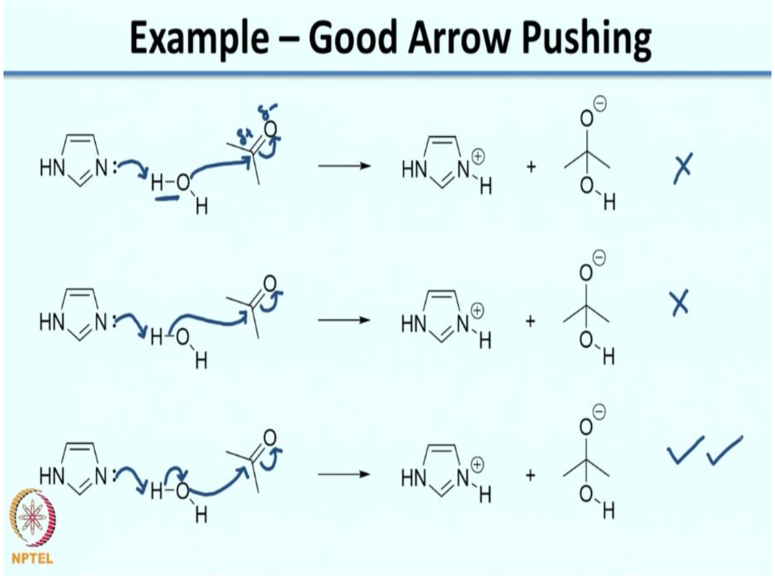

Example – Good Arrow Pushing

So, in this case my electron source is the lone pair on the nitrogen. So I can draw the arrow like this. Now what happens is sometimes people tend to just show the oxygen reacting with the electron deficient center here by showing the arrow from oxygen to the electron deficient carbon to give you the intermediate shown here and of course this would move here. Now the problem here is you have not indicated what happens to the electrons in this bond.

You have shown the nitrogen lone pair grabbing the proton, you have also shown the oxygen lone pair going to the electron deficient center but what is happening here? So this is not a good representation. Let us look at another example. Here again the first step is the lone pair grabbing the proton sometimes people show the bonded electrons going to the electron deficient carbon. This again is not a very good method of writing because you are showing the bonded electrons moving there which is not actually the case.

So a good way to push the arrows would be, you first show the nitrogen lone pair grabbing the proton. After that you can show the electrons actually coming to the oxygen from this bond. And then you can show the oxygen attacking the electron deficient carbonyl and finally the double bond of C=O moving such that the electrons come on the oxygen. So, this would be the best method to actually represent the transformation or reaction intermediate shown here.

So, now that you have a good idea about how to push arrows, I am just going to quickly go through the major types of polar reactions. You probably would have studied this in your 12th standard. But this would be a good refresher for you to make it easier for you to write reaction mechanisms.

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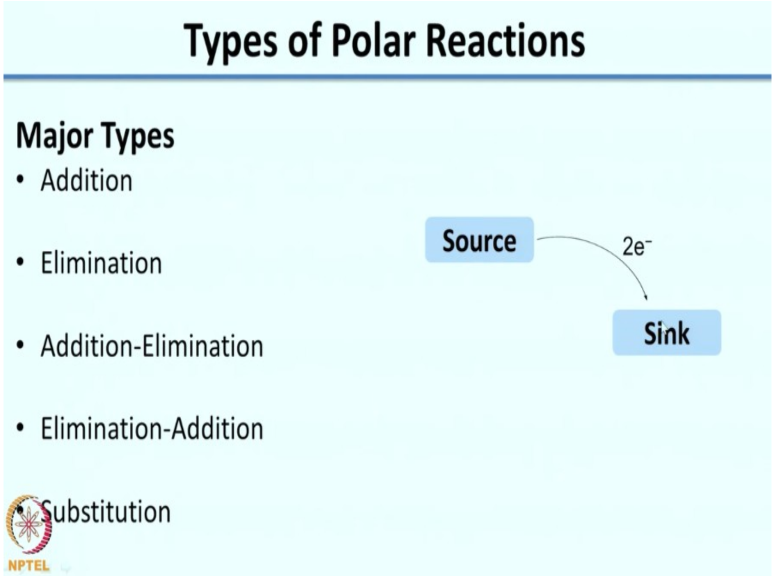

Types of Polar Reactions

Major Types

- Addition
- Elimination
- Addition-Elimination
- Elimination-Addition
- Substitution

Source

$2e^-$

Sink

So, I have broadly classified them as addition, elimination, addition-elimination, elimination-addition and substitution reaction and remember when you push arrows you talk about a source and a sink.

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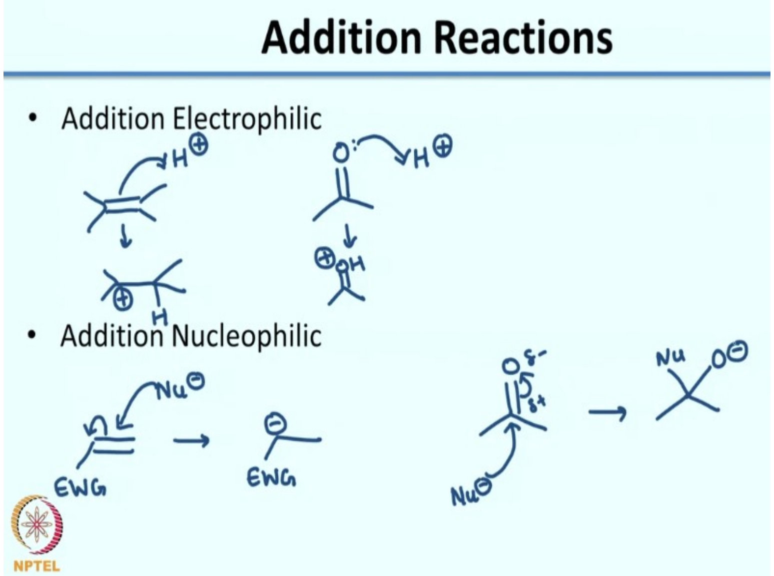

Addition Reactions

- Addition Electrophilic
- Addition Nucleophilic

So, let us come to the first class which is addition. You can again classify this as addition electrophilic and addition nucleophilic. So, one way is you can think of a double bond and when you think of a double bond you can think of the double bond actually grabbing an electrophilic species or a sink. So, here you have the addition to the double bond of an electrophilic species, so this is an example of an electrophilic addition. You can also think of a double bond like this.

So, when you looked at the aldol reaction in the acidic medium you can think of, so this would be an example of an electrophilic addition. So, in both these cases I will just quickly write what you get. So, in this case what you end up getting would be a carbocation and in this case what you end up getting would be a protonated ketone. The other example of addition would be a nucleophilic addition, so when you look at a nucleophilic addition,

again, you can think of a double bond which is electron deficient, so maybe you can think of an electron withdrawing group here and you can think of a nucleophilic species. Observe that whenever I am pushing the arrows, I am only pushing the arrows using the convention. So, you can imagine the nucleophilic species coming here and the double bond electrons shifting on this carbon.

So, what I end up generating would be a carbanion which is stabilized by this electron withdrawing group. Similarly, if I have a carbonyl group, again when you had looked at the aldol reaction you have δ+, you have δ- you can think of a nucleophile. The nucleophile would be coming to your electron deficient carbon center and what you would end up generating would be this tetrahedral intermediate.

So, these are examples of nucleophilic addition. I am not going to a specific reaction because mechanistically you can look at several different types of reactions which essentially have a similar mechanism where you have a nucleophile adding to a double bond or the double bond grabbing an electrophile. Coming to elimination reactions, this is again things that you would have studied in your 12th standard.

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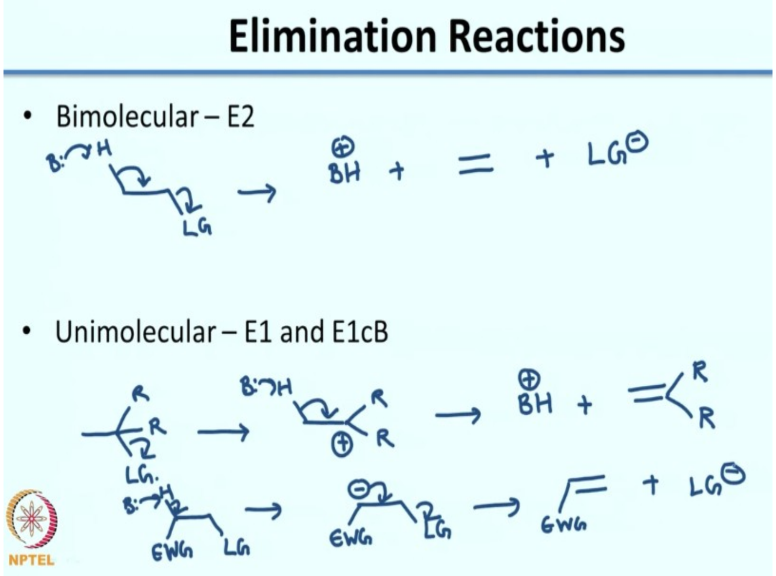

Elimination Reactions

- Bimolecular – E2
- Unimolecular – E1 and E1cB

One would be the bimolecular reaction which is typically called as the E2 mechanism. So you can think of, I will call this as LG which is your leaving group. So, you can think of a base grabbing a proton, these electrons will move here and the leaving group will leave. So, what you end up generating would be, again, if you notice here I have maintained the charge balance. I started with a neutral molecule and the net charge is maintained.

The other option is you can have a unimolecular reaction. The unimolecular can go either by an E1 mechanism or an even E1cB which is E1 conjugate base. So, in the E1 mechanism what happens is here again, you have a leaving group but what happens is instead of a concerted process you first have the leaving group leave. So, what you end up generating would be a cation and then you can think of elimination by after the neighboring proton is grabbed.

So, this is an example of E1 now in E1cB what happens is you have an intermediate which is stabilized, it is a stabilized conjugate base. So, you can think of EWG is an electron withdrawing group, a situation like this. Again you have a base, it grabs a proton, so you generate a negative charge which is stabilized by the electron withdrawing group, so this would be an example of E1cB.

Now substitution reactions are probably one of the first reactions that you would have studied. The bimolecular reaction, you would have studied the S_N2 reaction.

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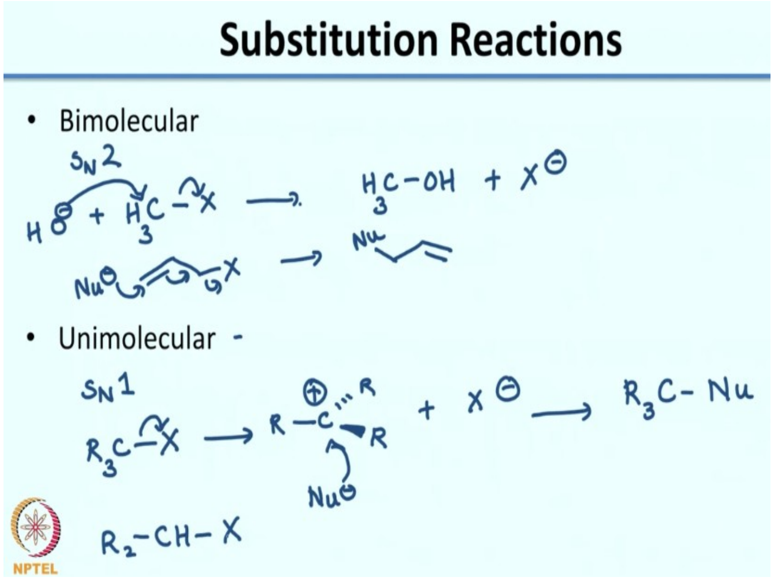

Substitution Reactions

- Bimolecular
- Unimolecular -

So, typically if I have reacting with, so you must have studied this, this is a concerted process and what you end up getting would be, so this is a standard example of S_N2, you can also think of a reaction like this. Now instead of your typical S_N2 reaction you have an allylic system, so you can think of a nucleophile adding in.

The other example is your unimolecular reaction which is S_N1, now typically the driving force for this reaction is formation of a stable carbocation. So, the first step is generation of the carbocation and in the next step what you have is you have your nucleophile adding in to give you the product. So, in both these cases although the net reaction is a substitution but the mechanism is very different depending on which substrate you choose.

So, for a reaction which involves a primary alkyl halide it undergoes the bimolecular reaction because in the transition state there is not much of steric crowding whereas in reactions which you have, for example formation of a stable tertiary carbocation it prefers to undergo the S_N1 reaction and if you have the formation of a secondary carbocation, so, for example if you have substrates like this, here you can actually find that the reaction mechanism depends a lot on what the R groups are and also what the reaction medium is and we will look at this later sometime during the course. Now the last class of reactions is, reactions that involve addition and elimination.

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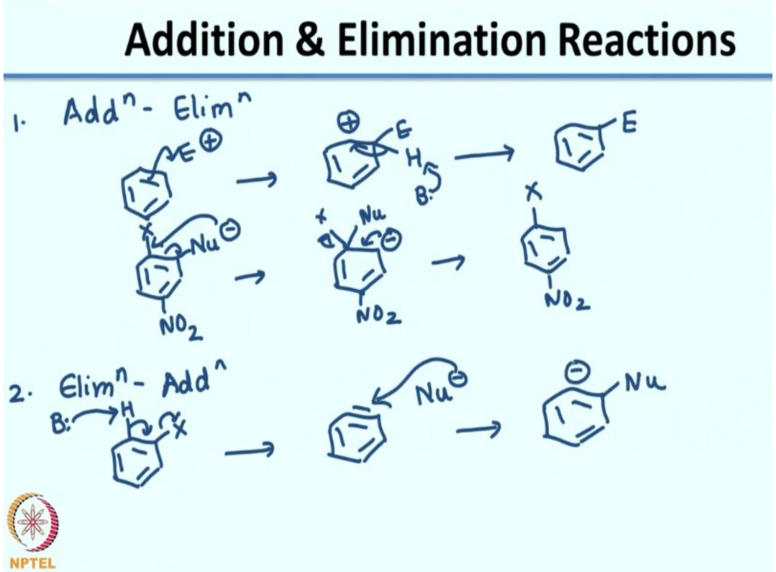

Addition & Elimination Reactions

So, there are two types of these reactions, one is the addition followed by elimination reaction and you must have seen this when you studied the electrophilic aromatic substitution. So, you can think of an aromatic ring interacting with an electrophile. So, the first step is an addition. Now once you have the addition reaction, the second part would be the elimination. So, you have the proton being grabbed to give you the product.

So, this is an example of an addition-elimination reaction. Similar to an electrophile, there is also the addition-elimination reaction involving nucleophiles. So, typically in this case you have the nucleophile come in to give you a charged intermediate, the negative charge is actually stabilized by an electron withdrawing group and then the next step would be elimination. So, these are examples of addition-elimination reaction.

You can also have elimination followed by addition and again a classic example is suppose you have say looking at an aromatic compound substituted by a halogen, so, if you use a very very strong base you generate what is called as a benzyne intermediate. Now this benzyne intermediate can interact with a nucleophile to give you the substitution product. So, this is an example of an elimination-addition reaction.

So, now before we stop this lecture, I would like to give you some more problems, these are very similar substrates if you look at or similar molecules if you look at what we have done here is.

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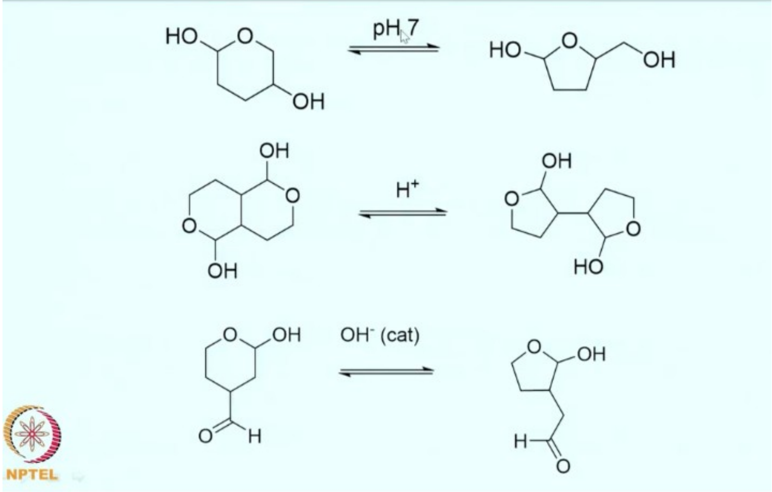
More Homework Problems



Now for each of these molecules, the reaction medium is different, so one is that a neutral pH one is at is at an acidic pH and the other is where you have a catalytic amount of OH^-. So, I would like you to look at these reactions and try to work these out yourself before we have the next lecture. And if you have any doubts please feel free to ask in the discussion forum where me or the TAs will help you solve these problems. Thank you.