

Concepts of Chemistry for Engineering
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Lecture 75
Elimination Reactions

Hello everyone, welcome to the module on Organic Reactions. In this module, we shall look at what are called as Elimination Reactions. But before we get going with the elimination reactions, let us just recap our memories on what we discussed under substitution reactions.

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Brief recap

1. Importance of studying organic transformations
2. Electrophilic aromatic substitution reactions
3. Nucleophilic aromatic substitution reactions
4. Nucleophilic substitution in aliphatic systems

So, in the last class, we had looked at what are called as organic reactions or organic transformations. And we briefly looked at the importance of organic transformations. And we said that the many of the things we come across in our day to day life are molecular origin and these in turn are made up of organic molecules. And in order to achieve a desired function, which could be a molecular motor, which could be a specific drug or any other kinds of an application, it is very important to make that molecule in high purity both chemical as well as stereo chemical. So, in that perspective, we had said that organic transformations are very useful and they tell us a lot about reactivity and selectivity of organic compounds. And then we had classified different reactions as addition reactions, elimination reactions, and substitution reactions.

And further we had gone on to look at what are called as electrophilic aromatic substitution reactions, where we said that a species which are electron deficient such as Br plus Cl plus or other electrophiles can attack on aromatic system like benzene or naphthalene to give a substituted products, which are actually steps in the multistep organic synthesis.

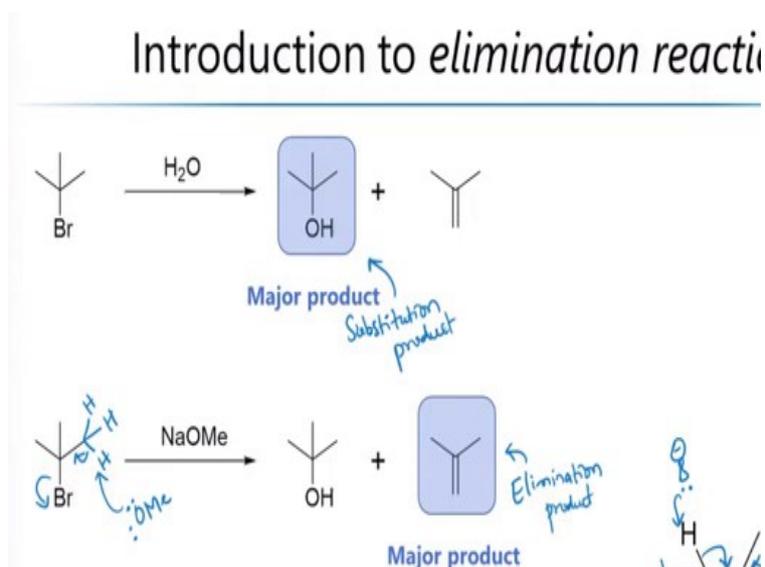
And similarly, we had said, we had looked at what are called as nucleophilic aromatic substitution here in place of an electrophile. Now, the nucleophile attacks onto the (benzene) onto the aromatic or it could be a benzene or any other aromatic system. But the distinction being the attack takes place on the position where the leaving group is there. For example, bromide or iodide or fluoride.

So, and that would lead to a substitution from our leaving group to incoming nucleophile that is what we had said in the case of nucleophilic aromatic substitution reactions. And we had gone on to look at substitution in aliphatic systems as well. And here we are classified two different mechanisms. One is called as an SN1 reaction, another is called an SN2 reaction.

And we had looked at the mechanism as well as the rate dependence on the both the base or the nucleophile as well as the substrate. And what we had seen is that these nucleophilic substitution reactions do depend heavily on the nature of the solvent as well the nature of the base or the nucleophile which is used.

So, we had not dwelled to that, but those are again important parameters to keep in mind when a nucleophilic substitution is being carried out. So, having said these things about nucleophilic substitution reactions, now, what we shall do is we shall continue the same discussion, but we shall now go into what are called as elimination reactions; that is reactions in which there is a loss of a leaving group in a reaction. So, let us go ahead and look at elimination reactions.

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I hope this reaction brings back your memories from the last lecture where you had seen the same tertiary butyl bromide being converted into the corresponding tertiary butyl in presence of water. But the only difference is we had not written the other product which is shown here, the alkene product. This is a possibility, but we had not discussed about this possibility in the last class.

If you now do the same reaction, if you do this reaction, the major product would be the tertiary butyl alcohol. And that is what we call it as a substituted product or a product obtained by substitution of the bromide for the OH group or the nucleophile in this case. However, if you do the same reaction, but under slightly different conditions, that is instead of using water if you use sodium methoxide again there are two possibilities are there; that is the tertiary butanol and the alkene.

But in this case what one observes is that now, you see that the alkene is the major product and this is what people would call it as the elimination product and alcohol is the substitution product. So, I hope you see the subtle difference in going from a substitution reaction to an elimination reaction, they look similar, but there is a subtle difference between them. And we shall try and look at why does this happen in a bit more detail.

But typically, what happens is instead of the sodium methoxide going and replacing the Br, it actually knocks out one of the hydrogens and lifts the formation of the alkene and I shall just

show you how that happens. So, if you take any of these hydrogens any of the three hydrogens which are present here or any of the (06:03), the sodium methoxide can go and attack on this and then the double bond shifts, the bond shifts here and then the Br leaves.

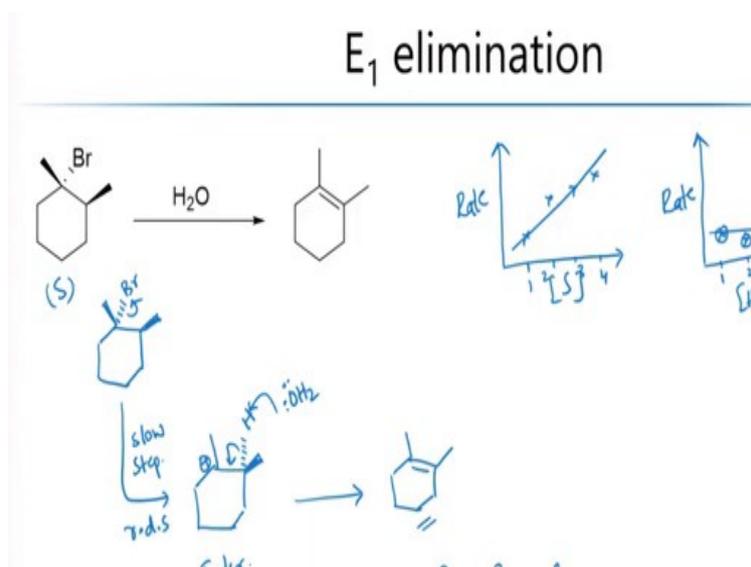
So, that would lead to the formation of the alkyne. And these are what are called as elimination product, this is what is called as an elimination product. And this is what is called a substitution product, this alcohol. So, I hope you can see that in a on the same substrate by just tweaking around with the nucleophile or which can also act as a base some time, you can get either a substitution product or you can get an elimination product.

And both of these depend heavily on the conditions one employs. So, having said this, let us look at what is a general living reaction or elimination reaction. So, in this reaction, typically what happens is you have a reactant or a substrate which is shown here like this, where these could be R and you have a base which comes and obstruct this proton, and this double, this bond moves to the between the two carbon atoms, and you have a now leaving group which goes away.

And that would lead to the formation of this kind of a product. So, R1, R2, R3, R4, and the minus leaving group. So, typically, the elimination reactions lead to the formation of the double bonds whereas the substitution reactions, you have a change of one group to the other, that is going to Br goes to the OH. So, I hope this gives you a general idea of an elimination reaction, where typically what happens is you have, if you call this as the alpha carbon, the carbon on which the leaving group is attached.

Then you have the beta carbon, hydrogen on the beta carbon is now obstructed by a base. And that leads to the shift of the bond between the beta carbon and hydrogen to the between the two alpha, between the alpha and the beta carbon and then the leaving group could leave to give the, to give rise to our double bond or an alkene. So, having looked at a general elimination reaction, let us go ahead and look at some of the mechanisms by which elimination reactions take place.

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So, here I had shown an example of what is called as an evil elimination. This is again very similar to the nomenclature which was used for the substitution reaction. Here E stands for the elimination, one is suggested that it is a unit molecular in mechanism. And in this particular substrate, a cyclohexane derivative gets converted into its corresponding cyclohexene. So, now let us go ahead and look at the mechanism of this reaction.

So, if you take the cyclohexane, you have a CH₃ and the Br, another CH₃, so this would be the first step it would leave giving rise to the formation of a Carbo cation, now the stereochemistry is lost at that particular center and now you have another hydrogen here and in the next step what would happen is, this is the slow step or what people also call this as a rate determining step.

In the next step you have the abstraction of the proton by the molecule of water and this moves here giving rise to the product and again what is important to note is that the mechanism is arrived by looking at what is called as kinetic studies or studies in which people have looked at how does the rate of the reaction vary when either the water or the concentration of the starting material let us say substrate S is varied rate.

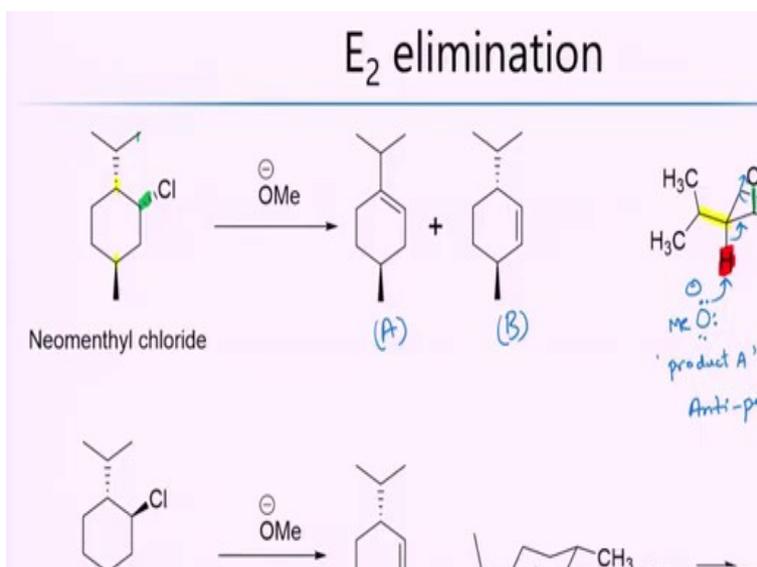
And as a function of concentration of S, one would observe a sort of almost linear dependence whereas if you now look at the rate with respect to the water it is invariant of the concentration of the water, these are just data points, so this would actually will lead you or this would suggest

you that the mechanism is involved only the substrate that is a bromine which one is investigating.

And the reason part of the reason why the elimination takes place first is that the generated intermediate Carbo cation this is stability of this is what is going to dictate whether the given reaction goes by an E1 or an E2 mechanism. If the generated carbo cation is stable, then one would follow an E1 mechanism where the bromide or the halide or any of the leaving groups would leave first giving rise to the Carbo cation.

And then a base would pluck hydrogen from the beta carbon to give rise to the corresponding alkene which is shown here. And typically, the stabilities of carbon cation is you have a third degree Carbo cation which is far more stable than 2 degree than primary and this would dictate the stability of the intermediate and ultimately, whether it is going to go via E1 or an E2 mechanism.

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So, now let us go ahead and look at what is called as an E2 elimination. So, as you might have already guessed, E2 again stands for an elimination reaction which is bimolecular in the rate limiting step this is analogous to the S_N2 reaction which we had seen where the rate determining step in the mechanism involved both the reactants. Similarly, in the E2 elimination mechanism here both the reactants that is the base as well as the substrate are involved and as a result, we call it as a bimolecular elimination reaction.

And this would become apparent as we go ahead and discuss a couple of examples. So, let us start by looking at this particular example of what is called as a Neomenthyl chloride right. So, if we take the substrate and subject it to a strong base like sodium methoxide or methoxide, what one observes is that there are two alkanes which are formed which is called as a one menthene and two menthene.

And you must be wondering why there are two products formed from the one given substrate. So, we shall look at that the origin of these two products and how that is related to the elimination reaction we are discussing. And the most interesting bit is if we now take the analogous compound that is menthyl chloride right, which has almost exactly the same structure except the stereochemistry on the carbon which bears the chlorine atom. What one observes is that exclusively the, two menthene product is formed.

So, this is where the stereochemistry becomes very, very important in the elimination reaction. And we shall try and understand this by looking at the conformations of the molecules. So, let us begin by looking at the conformation of the neomenthyl chloride first and then we shall go into the menthyl chloride.

So, if one draws the conformations of the new menthyl chloride, then what one can observe is the following; in the chair conformation of the cyclohexane. So, here you can see that the isopropyl group is in the equatorial position and the methyl group is also an equatorial position and the chlorine is in the axial position. So, just to make this the stereochemistry a bit more apparent, I will try and highlight the relevant bonds. I hope you can see that this one and this one.

So, if you now take a look at the isopropyl and the methyl in the starting material, I hope you see that the isopropyl that is this one and methyl and the isopropyl are actually trans with respect to each other that is, they would lie on the opposite side of the cyclohexene plane. So, indeed that is what we observe in this particular conformation, the methyl is pointing down and is an equatorial and this isopropyl is again in the equatorial, but it is now pointing upwards.

So, that means these two groups are now trans with respect to each other. And now, if you come to the other group that is the chlorine what one observes is that you see that the chlorine is now pointing up and the chlorine is a cyst with respect to the isopropyl and trans with respect to the methyl. So, let us see if that is indeed correct in this conformation.

So, if you now compare the isopropyl which is marked with yellow and the chlorine, I hope you observe that both of them are pointing upwards with respect to the plane of the cyclohexane. So, this suggests that the isopropyl and the chlorine are cis or they are on the same side of the plane.

So, that is in accordance with what we have in the starting material that is you have the isopropyl and the chlorine on the same side of the reactant. So, now once we have this what we can observe is the following. So, if I now highlight these two hydrogens here. So, now the incoming base the OME can come and pluck one of this proton and this one would move here and then the chlorine atom would leave giving rise to the product which is this, the B product.

And let us say we call this A whereas an equally likelihood possibilities that the OME minus would go and attack this hydrogen and again this would shift this bond here and then the chlorine atom would leave. So, this would lead to the pathway A or the product A and this would do the product B.

So, this is the reason why one observes both product A and product B in this reaction. And what is important to note is that the dihedral angle between the CH the CC and the CL or in other words the CH bond and on which the base or the OME minus is attacking and the CCL bond which is actually leaving they are at 180 degrees or the dihedral angle between them is 180 degrees and this is what people typically call it as a anti peri planar arrangement.

So, I will repeat it again anti peri-planar arrangement and this is very important for the elimination reaction to take place. And you will see in a minute how this anti peri-planer arrangement or the lack of it leads to the regio chemistry in the products. So, if now come to the next one that is the menthyl chloride example.

Here the two conformations which are possible are easy much easier to visualize than the case of the neomenthyl chloride. So, here what one can see is that the all the three groups that is the isopropyl, fluoride or the methyl can be in the equatorial position and this will be the most stable energy confirmation because you have the least amount of repulsions.

However, you can also go to the other confirmation in which all these three groups are in the axial position by doing a ring flipping, but then this will be a high energy conformation of the

system. So, in this case if I now take the, if now the OME comes and attacks So, let us say the (())(20:31) one possibility is it attacks this hydrogen and then the hydrogen this one will move here and then the chlorine atom would leave and this would lead to the formation of the product which is shown here that is the two menthene.

So, if you now look at the confirmation on the other carbon that is on the one side of the chlorine you have a hydrogen which is trans with respect to the chlorine or in other words anti peri-planer. But if you now come to the other side, you will have the hydrogen which would be here right in the equatorial position. So, this is actually not in the correct orientation or it is not anti-peri-planar with respect to the chloride.

As a result, this hydrogen would not undergo an elimination to give rise to the one menthene or the product A which was possible in the above reaction with the new methyl fluoride. So, I hope you see that the arrangement of the hydrogen or the beta hydrogen on which the attack by the base takes place that is in this case, the hydrogen shown here and the chlorine atom or the leaving group should be at an dihedral angle of 180 degrees.

Or in other words, they should be anti-peri-planner with respect to each other. So, this would facilitate the elimination reaction. However, if such an arrangement is not possible, then elimination reaction by an E2 mechanism does not take place. So, that is also the reason why although the confirmation which is shown on the left-hand side that is this confirmation is more stable.

It does not undergo reaction because the orientation of the chloride that is the leaving group and the hydrogen on the beta carbon are not anti-peri-planar. So, a consequence of this is that neomenthyl chloride in which the most stable configuration or the most stable conformation has to two hydrogens which are anti-peri-planner with respect to chloride, reacts roughly about 40 times faster compared to the menthyl chloride in which the favorable conformation does not have an anti-peri-planner arrangement.

So, in essence, what we are trying to say is that in a E2 elimination, the stereochemistry or the arrangement of the leaving group, and the hydrogen on which the base attacks is very critical to observe the product and that dictates the ratio as well as the or the regeo-chemistry of the product

which one observes. So, with this, we shall now try and compare the E1 and E2 elimination reactions and see what are the commonalities of the differences between them.

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Conditions	E ₁ elimination	E ₂ elimination
Rate law	Unimolecular (only substrate)	Bimolecular (su the base)
Nature of the halide	Faster with tertiary > secondary > primary (stability of carbocation)	No dependenc
Base	Weak	Strong
Stereochemistry	No dependency	Anti-periplana

So, with respect to the rate law, what you see is that even is a union molecular that is it depends only on the substrate, leaving group leaves first to give us the formation of the carbo cation. So, it is a union molecular reaction, whereas E2 is a biomolecular reaction where both the base as well as the substrate take place in the rate determining step of the reaction.

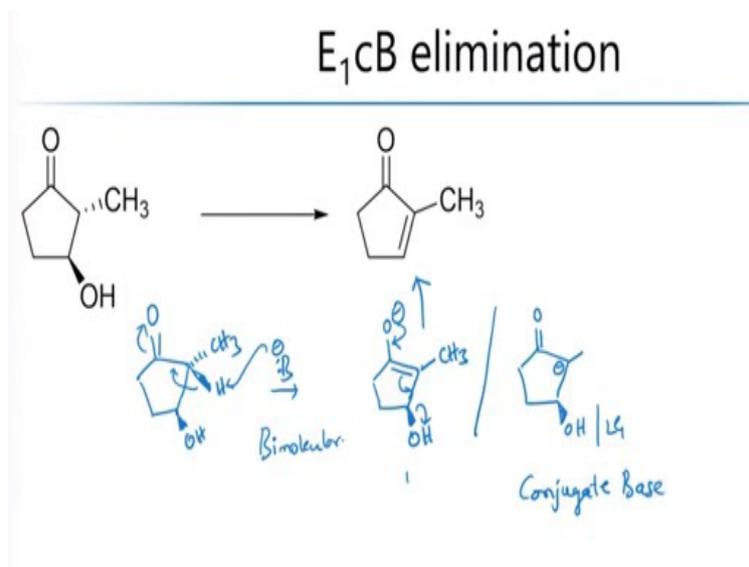
And coming to the nature of the halide, what one observes is that the E1 is faster or it is much more facile when the halide is a tertiary or a secondary because the Carbo cation generated is consequently far more stable whereas no such dependency is observed in the case of the E2 elimination.

And in case of even the base has a very, not significant role that is it can it will just abstract the proton after the rate determining step and as a result, the base is invariably a weak base whereas in the case of an E2 elimination, a strong base is used and this strong base, plucks the proton in the rate determining step.

And lastly, most importantly, E1, in the E1elimination, there is no dependency on the stereochemistry of the substrate. Whereas in case of E2 elimination, an anti peri-planar arrangement of the living group is necessary to obtain the desired double bond or the elimination

product and these are the two most commonly observed kinds of mechanisms which the elimination reactions undergo.

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In addition to this there is one more kind of mechanism which is called as an E1 CB and we shall be just briefly look at that and here what we observe is that if you take a substrate like this the cyclohexene is a known derivative and if you subject to a mild base and just write down the substrate once again, if you subjected to mild base this is what one would observe or this is also typically written in a slightly different form that is. You can write them in two different forms because there is; one can convert between them by using resonance and once this is, this one is there then the minus would come down and then you would have the leaving of the OH minus and that would lead to formation of the product here.

So, this kind of mechanism where first base abstract proton on the beta, be on the beta carbon and then generates anion, carbon anion here like this and this carbon anion further undergoes a reaction or further helps in the elimination of the leaving group to give rise to the product is called as an E1 CB. Here E1 CB stands for elimination uni-molecular but conjugate base that is also the first reaction this is a bimolecular reaction.

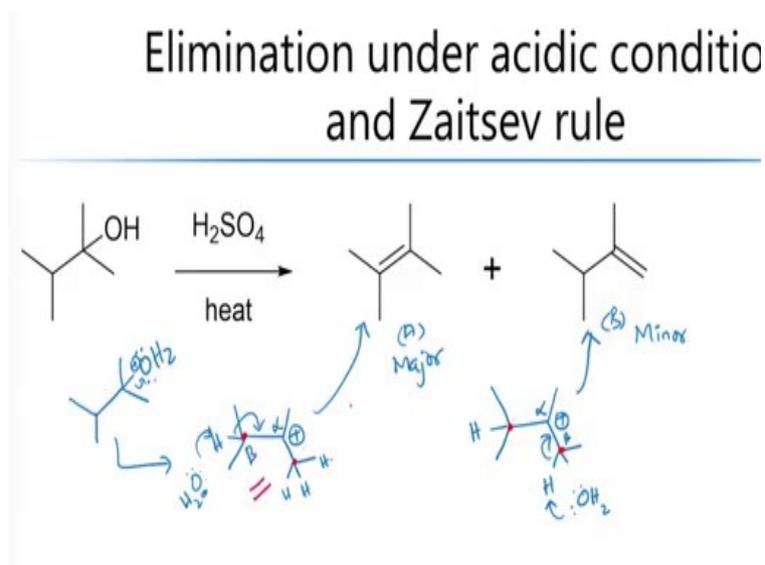
This could be one can think of this as a bimolecular reaction, but this is typically fast. Once this happens you generate the carbon ion and this carbon ion is the one which is going the

elimination reaction that is you have the negative charge comes down and leaving group in this case this is the which goes away to give rise to the product.

And since all of this occurs in the same molecule that is once you form the conjugate base that this is the conjugate base here in this particular reaction and once you form the conjugate base that would further undergo elimination to give rise to the product. So, as a result this mechanism is typically called as E1 CB that is elimination uni molecular conjugate base.

So, again reiterate elimination is apparent and it is uni-molecular because it takes place in this conjugate base form where you do not need any other reactant and since you have a conjugate base which is, which give rise to the product you add the CB to indicate that the mechanism involves a conjugate base. And I hope you can note the difference that this E1 CB involves on carbon ion intermediate compare to E1 which involved a carbo cation and E2 which did not involve any charged intermediates.

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And finally, we shall look at what is another kind of elimination which typically takes place under acidic conditions and an example of that is shown here and that leads us to what is called as Zaitsev rule. So, if one takes this particular molecule which is shown here the alcohol which is shown on the left-hand side of the arrow and if you subjected to a slightly acidic conditions and heat then what typically happens is the following; that you would have the OH getting protonated and then then this would first leave to give rise to a carbo cation.

So, now this Carbo cation can undergo loss of proton that is elimination to give rise to both these products which are shown here that is A and B, so let us say if I call this alpha and if I call this beta, there is also another proton here or I can look at these protons, any of these protons, if the, if we have the loss of the beta protons, then we will would product A, if this is lost, then that would lead us to the product A, whereas, I will just redraw this again.

Whereas, if any of these protons are lost, it will lead us to the product B. So, yes, obviously, there will be a base or a solvent which would pluck away these protons, though and that would lead to the formation of the product elimination product which one observes. So, now the interesting bit is you have both the products A and B which are possible.

However, the product which is observed in majority is A, A is the major product and B is invariably the minor product and this is what is also termed as that Zaitsev rule or in other words, the elimination occurs such that the hydrogen is removed from the beta carbon with the least number of hydrogens.

So, that is what is being shown yet that is there are two beta carbons like for example, we had shown one beta carbon is this, another beta carbon is this that I will just marked with a different color, so one beta carbon is this, another beta carbon is this. So, you can have loss of proton from both of these carbon atoms.

But what does Zaitsev rule tells us is that the loss will take place from the carbon which has the least number of hydrogen atoms that is in this case, the this particular the carbon and that leads to the product A which is a major product or a simpler way of looking at it is, in an elimination reaction the product which is formed is the more substituted alkene.

So, this is because of the stability of the internal versus the terminal alkyne which is being formed. So, with this, we shall stop our discussion on the elimination reactions. And in the next lecture we shall look at what are called as addition reactions and oxidation and reduction reactions. Thank you.