Concept of Chemistry for Engineering
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Lecture 76
Addition, Oxidation and Reduction Reactions

Hello everyone, welcome to the module on organic reactions. In this lecture, we shall look at what are called as addition reactions, oxidation and reduction reactions. But before we get there, let us just quickly recap what we had learned in the previous class.

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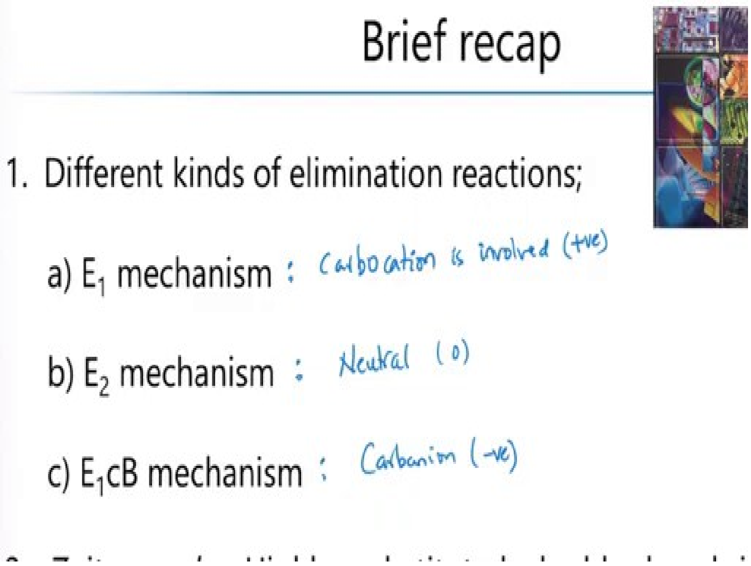

Brief recap

1. Different kinds of elimination reactions;
   - a) E_1 mechanism : Carbocation is involved (+ve)
   - b) E_2 mechanism : Neutral (0)
   - c) E_1cB mechanism : Carbanion (-ve)

In the previous lecture, we had looked at different kinds of elimination reactions, that is, why, E1 mechanism, E2 mechanism, E1 cB mechanism and we had also said looked at something called as Zaitsev rule. So, in the we had said that in E1 mechanism a carbocation is involved. So, just to make a clear I shall write down that, so in a E1 mechanism a carbocation was involved and E2 mechanism was almost a neutral and E1 cB involved a carbanion.

So, this is a positively charged and this is pretty much zero and this was a negatively charged species which is involved and we had said that the E1 mechanism takes place it is a unit molecular mechanism and typically the alkyl halide or the compound bearing the leaving group is very-very important in the sense the whether the carbon is tertiary, secondary, or primary dictates whether the given mechanism goes by an E1 or E2.

And in the case of E2, we had said that the stereochemistry of the hydrogen on the beta carbon is important or in other words, anti peri-planar arrangement is necessary for elimination in the B2, in the E2 mechanism is what we had said. And finally, coming to E1 cB here we had seen that on the hydrogen on the beta carbon gets obstructed by a base to give rise to a carbanion.

And this carbanion on the beta carbon is stabilized by some groups which are present on the beta carbon that is the reason why this carbanion forms in the first place. And then this carbanion further undergoes reaction to kick out the leaving group and form a alkyne or a double bond. And we had also seen examples in which not examples in which not an alkyl halide but if an alcohol is present by adding a mild acid and heating the reaction mixture, one could obtain an elimination reaction or elimination products.

And here we had come across what is called as a Zaitsev rule; where what, where we had said that among one or more alkyne possibilities, the one with the highest substituents is the major product or in other words alkyne which is highly substituted will be the major product. And this is primarily because if you look at the substitution on an alkene, if there are more carbon-carbon bonds that means the stability of the compound is far more compared to c-ch bonds or the compounds contains c ch bonds.

So, because of this thermodynamic driving force, the double bond with the maximum number of substituents will be the major product in the elimination reaction and this is what was termed as Zaitsev rule, alright. So, now, what we shall do is, we shall go ahead and look at what are called as addition reactions and oxidation as well as reduction reactions.

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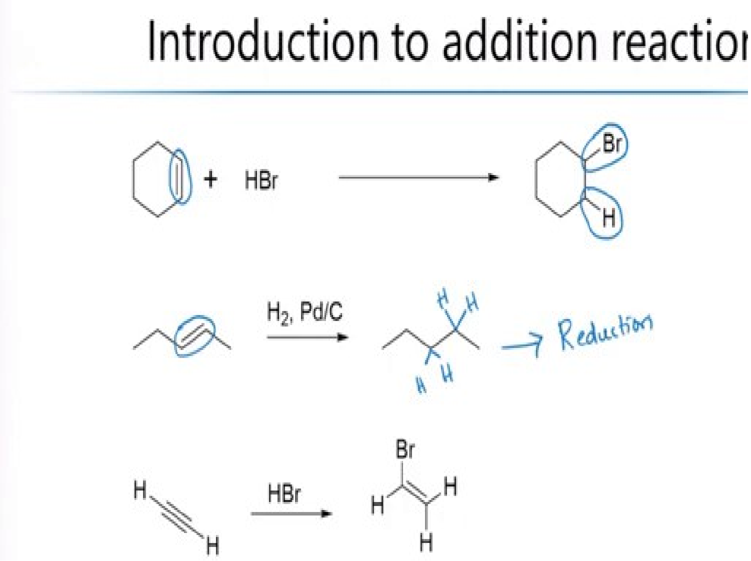

Introduction to addition reactio

So, to begin with the addition reactions, I am sure you all remember this reaction which we spoke a couple of class ago, where what we said is that, there is a double bond a cyclohexene to which HBr gets added that is both hydrogen and the bromine gets added across the double bond to give rise to this product, Bromo-cyclohexane. And one can think of many such examples where if you take an alkene and subjected to conditions of hydrogen gas or palladium carbon catalyst, one would get the corresponding alkene.

Here again, across this double bond, two hydrogens are added. And similarly, if we take the alkine and add an HBr, the both hydrogen and the bromine adds across the C triple bond C to give rise to an alkene, which is shown here. So, in essence, what we are trying to do in addition reaction is we are actually trying to break a Pi bond and add or form to new sigma bonds. So, just to illustrate that, I will show you when these reactions, what kind of bonds are broken and what bonds are being formed.

So, if you take the first example, you have a Pi bond here which is gets broken between the, these two carbons, and we have these two new sigma bonds that is C-CH and the CBr which are being formed. And this is a typical feature of addition reactions. And one can see this in many kinds of addition reactions. So, if we now look at this hydrogen, here again you have a double bond or an unsaturated bond.

And if you now, look at this, you have two CH2 here, or two hydrogens, and here again you have two hydrogens. So among them, you have found two new CH bonds compared to the reactant. Similarly, one can also look at the last example as well. So, in essence, in an addition reaction, we break one or more Pi bonds and form two or more sigma bonds in the product. So, this is what one would call typically called an addition reaction.

And these classifications are not exactly or strictly sharp. By that I mean, if you look at this second reaction or this particular reaction, people also call this as a reduction. So, the reactions what we are looking at might be classified, a same reaction might be classified under one or more heads, but the principle remains the same that is, in this case, a pi bond is broken, and more than two or more than two of the sigma bonds are being formed.

And such reactions we call them as addition reactions. And if you now take this argument further, one can look at two different kinds of examples. And let us first begin by looking at reactions in which there is a possibility of one or more product and where the products are constitutional isomers of each other. I hope you remember from your lectures on stereo-chemistry, what do you mean by constitutional isomers and stereo-isomers.

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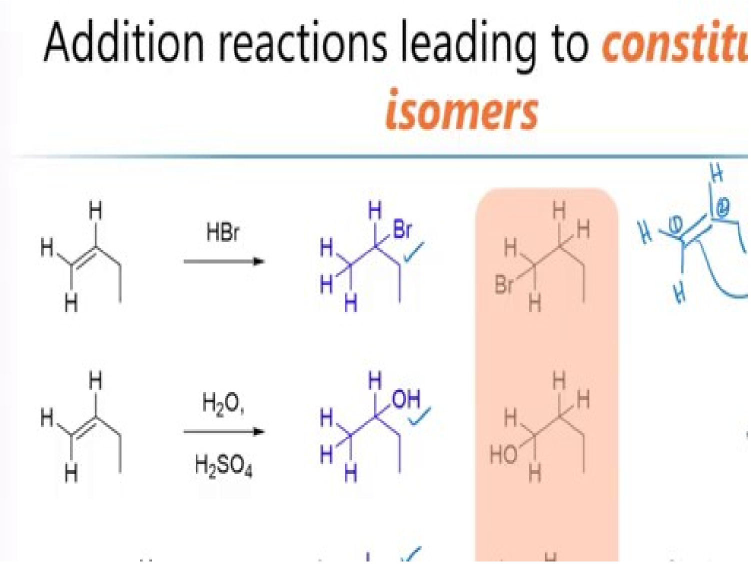

Addition reactions leading to constit
isomers

So, let us take one of the examples where again we have a double bond which is shown here or an alkene to which HBr can be added. So, the hydrogen can be added on the first carbon or on the second carbon as well. And that leads us to two different kinds of products in shown in either blue or grey color. And similarly, if you take the same alkyne and subject to an acidic conditions, you can get what is called as an hydration reaction or addition of an OH bond and a hydrogen across this double bond to give rise to this alcohols.

Again, two kinds of alcohols are in principle possible. And finally, if you take again an alkyne, and try to add an HI across it, you can again get two kinds of products which are again now constitutional isomers of one another. That is an important thing, which I want you to note. Let us see how these isomers are possible. I will show you for the first example and the principle remains the same for others as well.

So, if you take this, *the starting material*, that is you have a double bond and then hydrogen and then ethyl group. So you have an HBr, so you have an H and Br so this is typically a polarized H plus Br minus and this double bond goes and takes away, takes this that could lead to two possibilities; one is, so if I call this 1 and if I call this 2; hydrogen can go to the carbon 1, and that would leave with this carbocation or you could also have another scenario which is you can have hydrogen gets transferred to the second carbon.

And you can have this 1, 2. So you can have these two possibilities. So if you now look at the stability is a Carbocation I am sure you will agree that this is a far more stable or more stable Carbocation and this is a less stable Carbocation. As a result once this forms then the attack by the OH minus or the Br minus becomes facile and that would lead to the major product that is these, the blue ones in this case.

Whereas, if you look at the other possibility which is shown here which is the constitutional isomer these are typically what is called as a minor product or they are formed in very less quantity. So, just to make it more clearer So, these are all minor products whereas, all of these are major products, okay, the ones shown in blue are the major products, the ones shown in grey are minor products.

And I hope you see the reason for that because that stems from the stability of the Carbocation or the intermediate. So, this now beautifully shows you how a simple addition reaction can give rise to two constitutional isomers and the stability of the product is now dictated by the stability of the intermediate.

Similarly, the addition reactions can also lead to stereoisomers in principle, but many of the times the reactions go to exclusively one of the stereoisomers and we shall look at a couple of examples of such case.

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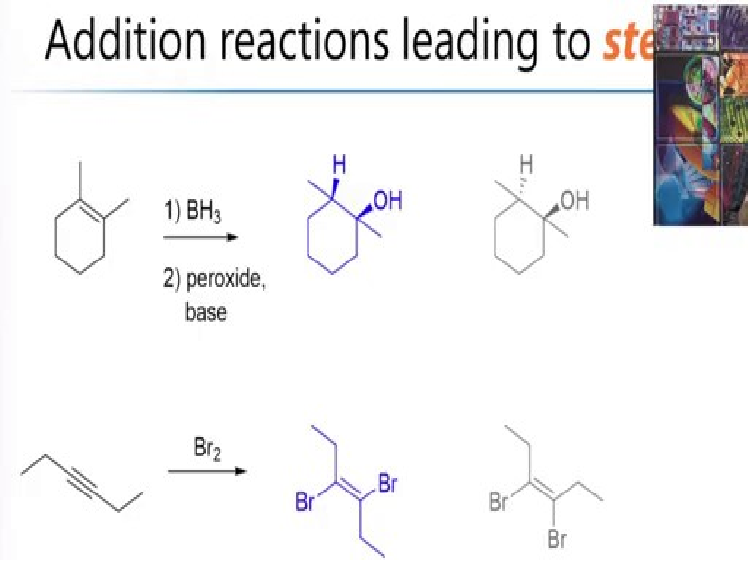

Addition reactions leading to ste

So, here you see a reaction where a cyclohexene derivative reacts with the BH3, a peroxide and a base to give rise to the corresponding addition product where across the double bond and OH, an hydrogen is added.

And what you see is that you can get both the di stereoisomers the product. However, exclusively the one in blue is observed. And that is because the reasons that is because the sterical arguments in which the reactant the other reactant goes and approaches to give rise to the product. And similarly, if you now take an alkyne which is shown here and add a bromine you can get two kinds of the brominated products; that is 1-2 di-bromo compound where the 1-2 compound is either in the trans configuration or it is also can be in the cis.

So, between the cis and the trans; the trans is exclusively observed because the bromine and the alkyne initially forms a three membered ring and this is opened by attack from the backside to give rise to the trans product. So, that is why you exclusively obtained the trans product in this reaction and no or very little of the bromine of the cis isomer is observed.

So, I hope you can see that addition reactions, simple addition reactions can be useful to prepare exclusively a single stereoisomer or even a pair of constitutional isomers with different stabilities. So, now, we shall go ahead and look at what are oxidation and reduction reactions in organic chemistry and how to understand them and few examples of such reactions.

Alright, so if you now start looking at oxidation reduction reactions in organic, in organic reactions. So there are, there is a simple thumb rule which is used to understand whether a reaction is undergoing oxidation or reduction. So, let us first look at the rule and then we shall look at some of the oxidation or reduction reactions.

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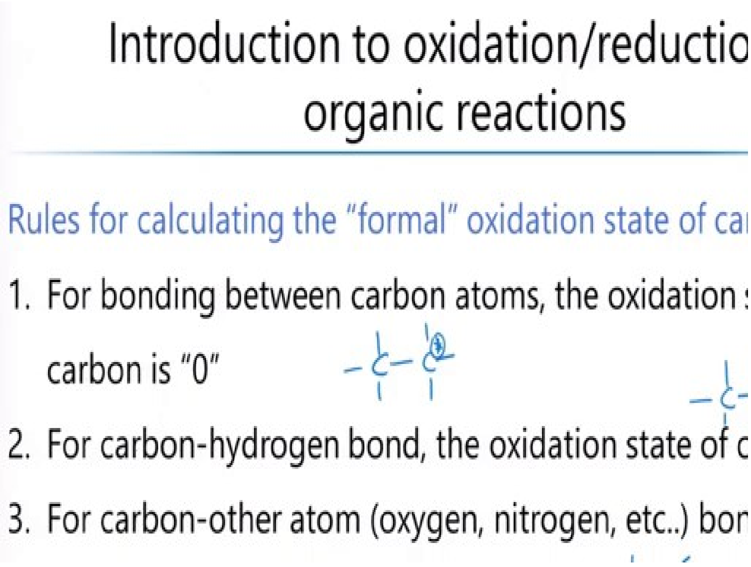

Introduction to oxidation/reductio
organic reactions

Rules for calculating the "formal" oxidation state of ca

1. For bonding between carbon atoms, the oxidation
   carbon is "0"
2. For carbon-hydrogen bond, the oxidation state of c
3. For carbon-other atom (oxygen, nitrogen, etc..) bor

So, the rule uses calculating the formal oxidation state of the carbon and once you calculate the formal oxidation state of the carbon, then based on the change in the oxidation state of carbon, you can conclude whether the reaction is undergoing oxidation or reduction. This is very similar or analogous to what one would encounter in inorganic chemistry, where if you say iron goes from plus 2 to plus 3 or plus 2 to plus 1.

You would call them as oxidation or reduction respectively. Similarly, here, we shall first look at the rules by which the oxidation state of the carbon is being ascertain. And once we ascertain that then we can decide whether the reaction we are looking at is an oxidation or a reduction reaction.

So, the first rule is that if the carbon is bonded to another carbon atom, then we assume the contribution of the next carbon atom as being 0. Let us say if you are interested in looking at a carbon bonded to another carbon atom. Like in this particular case, this if you want to look at this carbon atom, you see that it is bonded to another carbon atom.

Since the electronegativity is the same for two carbon atoms, we give this contribution of the next carbon atom on the alpha position we give it as a zero value. And now, if we go to a carbon-hydrogen bond, then we give you an oxidation state of carbon, we assign it as minus 1. So, the reason is or the so if we now take C-H, okay. So, the carbon is more electronegative compared to hydrogen.

So, as a result, we give a minus charge to the carbon if it is attached to as hydrogen. And if there are more than one hydrogen, then we multiply this by the number of hydrogens present. And if now go to other atoms that is carbon bonded to other more electronegative atoms that is oxygen, nitrogen or other atoms, then we give a formal oxidation state of carbon as plus 1; that is if I have a C-O bond, C-O or then this carbon, this particular carbon, we can give it as plus 1, because it is now bonded to a more electronegative atom, which is oxygen in this case.

So, these are the rules which one would use to calculate the overall oxidation state of a given carbon atom. And once you have that, then we can ascertain whether the given reaction is an oxidation or reduction reaction. So now let us go ahead and take a few examples to see how this actually works.

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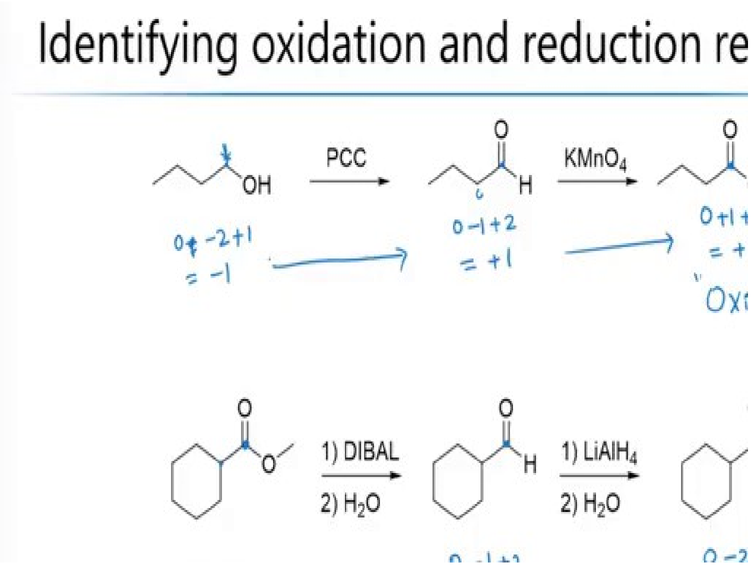

Identifying oxidation and reduction re

So, here is a sequence of reactions which is drawn or shown in front of you, where we have an alcohol which gets converted into an aldehyde by using what is called as PCC, PCC is nothing but a peridinium chloro chromate, a reagent, which is used to selectively oxidize alcohols, primary alcohols to the corresponding aldehydes.

And then if you take that aldehyde, and treat it with the potassium permanganate or a chromate, you would get the corresponding carboxylic acid. So now let us do this exercise to see whether this is an oxidation reaction or a reduction reaction. So for that, we would be interested in looking at this particular carbon atom that is this atom. So I will start writing out the all the contributions.

So, now it is connected to one carbon atom on this side. So the one contribution is first is 0, and it has two hydrogens, so then I would write that as minus 2, and it is connected to one oxygen, so I would give it a plus 1. So this will be in total minus 1 oxidation state of this particular carbon.

Similarly, if I look at the oxidation state of this carbon, so one is 0, because it is connected to carbon on this side, and connected to hydrogen on the other side minus 1, and it is connected to oxygen, since it is a double bond, I will multiply it by 2. And I am going to write it as plus 2, because oxygen is more electronegative than carbon.

And this would give me a plus 1. And if I now come down and try to do the same exercise for this, what I see is it is connected to again, a carbon atom, I will put it as 0. And this is connected to one oxygen, so plus 1. And this is again connected to two via double bond to an oxygen, so I would write it as plus 2, and this would go to plus 3. So here, you see that the change in oxidation is from minus 1 to plus 1 to plus 3.

So now the, since you are going from minus 1 to plus 3, or you are going to more positive state of oxidation, you would call this typically is an oxidation reaction. So thus, we can call this as an oxidation reaction. And similarly, let us take another example, where we have a cyclohexane derivative and let us try and do the same exercise with this and see what comes out of this.

And here I will be interested in looking at this particular carbon. And if we now take this particular carbon, it is again attached to one carbon on this side this carbon, so I shall put 0 as the value and one other substituent is an oxygen, so plus 1. And it is again attached to C double bond O that means plus 2. So, this would give rise to plus 3 and if I come to the middle product which is an aldehyde so I am going to again look at this.

So, I have a attached to carbon, so I will put this as 0, and attachment to one of the hydrogens minus 1, C double bond O plus 2 and this would give me a plus 1. Finally, if I come to the alcohol this carbon is now attached to one carbon, which is 0, two hydrogens minus 2 and plus 1 because it is connected to one oxygen atom. So this would give me minus 1.

So, if we now look at overall what is happening; you are going from a positive oxidation state, and it is getting reduced to minus 1, you are going from plus 3 to minus 1. That means you are undergoing a reduction reaction in the classical sense which one would use for an organic which one would use for inorganic complexes.

So, this, I would call it a reduction reaction. And in all this, while you might have already noticed that I had written something called as DIBAL, I have written something called lithium aluminum hydride, so these are specific reagents, which one uses to carry out a specific transformation that is reduction from an ester to an aldehyde, or an aldehyde to a corresponding primary alcohol.

Similarly, on the top scheme, you see that PCC is used for a selective conversion of the alcohols, primary alcohols to the corresponding aldehydes. And it only stops the oxidation state at the aldehyde it does not lead to the overall oxidized product that is carboxylic acid. And there are n number of such reagents which one can use to perform these oxidation, reduction or any kinds of transformation selectively.

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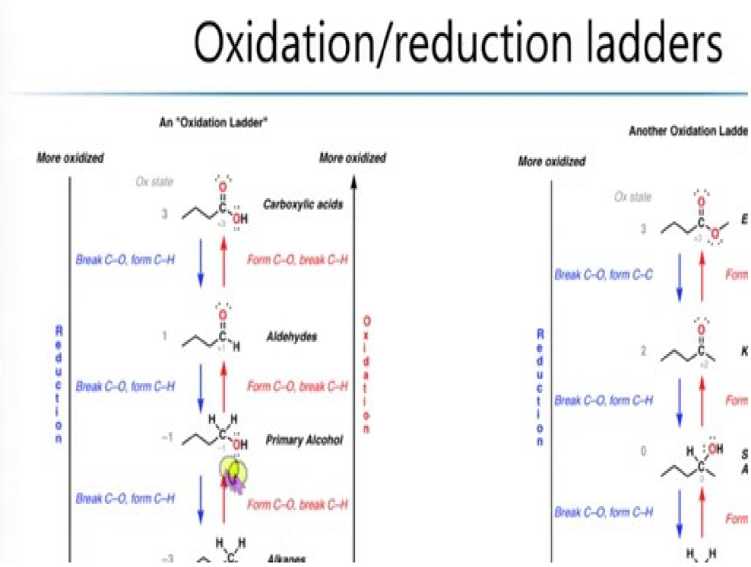

Oxidation/reduction ladders

So, with this I will leave with what are called as oxidation reduction ladders. And this is something which I have taken from the website called master organic chemistry, which is very beautifully explained for a beginner. And what you observe here is that here a primary alkyne is shown here. And on the right hand side is shown as the oxidation and on the left hand side is the reduction.

And you see the oxidation state of the carbon going from minus 3 in alkane to minus 1 in primary alcohol and goes to plus 1 in the aldehydes and plus 3 in carboxylic acids. This is something which we saw. And if it comes from the other side, you undergo a reduction that is exactly what is shown here.

And one can do the same exercise even for secondary alcohols that is going from alkyne. If you go to secondary alcohol, and then to ketones and then to esters, one can do the same exercise. And then you see these beautiful charts or ladder diagrams, which give you the relationship between oxidation and reduction.

And one can also see that here there are again some of the reagents for oxidation reduction which I have mentioned here, that is sodium borohydride, lithium aluminum hydride, which are reagents which are known to transfer what is called as an hydride to accomplish these reduction reactions.

And then you have oxidants such as again PCC that is pyridium chloro chromate and H2 CR O4. that is the chromium salt. And the same kind of examples can be used to carry out the other transformations as well. So, I hope that this has given you some idea of what do we mean by addition and oxidation and reduction reactions.

And this also I hope you are given an idea about some kind of reagents or specific reagents which are available for transforming an alcohol to say an ester or to or to corresponding primary alcohol to an aldehyde or aldehyde to carboxylic acid. So there are various reagents around in the literature. And based on the transformation which one is interested, you can choose the appropriate reagent and carry out the transformation.

So, I will just put this thing whatever we discussed in a nutshell, that is, we started out by saying that organic reactions are important because the world which we live in is a molecular world. And that hinges critically on the molecules which one can make. And in order to make the molecules one must understand the chemistry which is happening behind it.

So, in that perspective, we started looking at different kinds of organic transformations. And we had looked at substitution reactions, where one can transform benzene into various kinds of derivatives. It could be either a chlorobenzene or a nitrobenzene or any other kind of benzene and similarly, we had seen substitution in aliphatic systems, where a living group could be replaced with an incoming nucleophile via different kinds of mechanisms to give rise to substituted product.

And then we had seen what are called as elimination reactions, where you buy, where a leaving group leaves to give rise to a double bond. And finally, in this lecture we looked at oxidation reduction and addition reactions. So, these are some of the tools which synthetic organic chemists would use in our day to day lab to prepare a molecule or a drug of interest.

And invariably, the synthetic transformation would involve more than one step at a time that is one has to carry out series of transformation to arrive at a particular molecule of interest. And that molecule is what is going to be ultimately used in any of the devices or drugs. So, I hope this has given you some flavor of organic transformations and their relevance in the day to day life. With this, I shall stop here and thank you for listening to me.