Introductory Organic Chemistry
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Lecture – 46
Alcohols Part - 01

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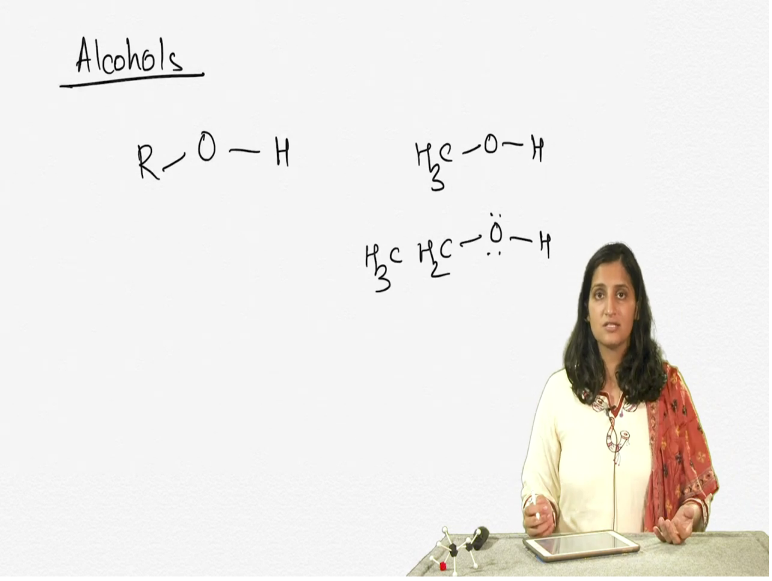

Today we will begin looking at Alcohols as functional groups. Now, alcohol as a functional group R-O-H, R being any alkyl group is such that the R group, which is an sp^3 hybridized carbon, is attached to an oxygen and that oxygen is attached to a hydrogen. So, I can summarize alcohols as ROH and R being for example, methanol or ethanol, right; wherein sp^3 hybridized carbon is attached to an oxygen, oxygen is attached to a hydrogen, right. Oxygen also has two lone pairs of electrons, which will play role in most of the organic reactions of these alcohols.

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For example, here I have a model of isopropanol and you can see that this is the oxygen for example, attached to the hydrogen. And this oxygen is attached to the central carbon, the central carbon is sp^3 hybridized it is forming a tetrahedral geometry and that’s how isopropanol will look, right. Isopropanol by the way is used as a rubbing alcohol in medicinal industry. And it is by the way one of the most used alcohols as a disinfectant because of its low toxicity in the medicinal industry, okay.

So, if you really pay attention to this the bonding angle for this oxygen is kind of close to a tetrahedral angle. In fact, for methanol it is very close to 108.9 degrees kind of very close to a perfect tetrahedral angle of 109.5 degrees. So, you can imagine that all the atoms here are close to a tetrahedral geometry.

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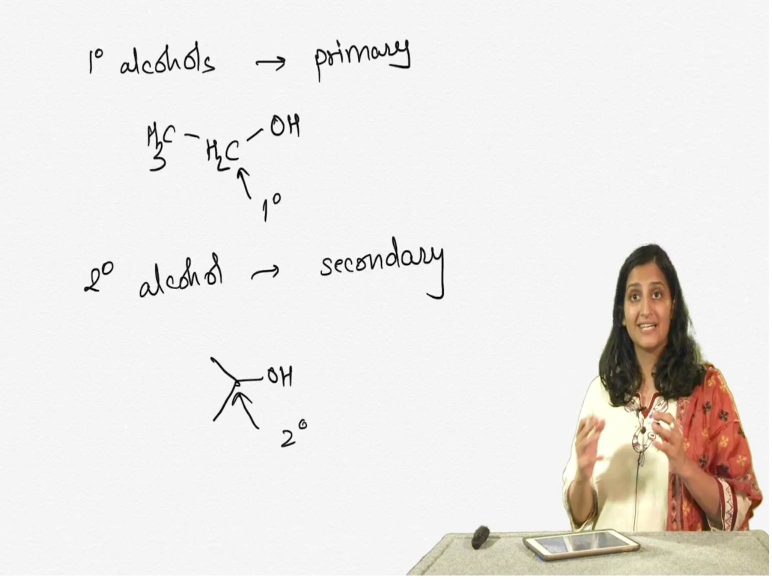

We also classify alcohols as primary, secondary or tertiary alcohols. So, primary alcohols are the compounds where the OH group is attached on a primary carbon meaning for example, ethanol is a primary alcohol because this is primary carbon, right. A secondary alcohol will of course, have a secondary carbon. So, for example, the one I have in my hand, isopropanol is a secondary alcohol because the carbon that the OH is attached to is a secondary carbon; it is attached to two alkyl groups.

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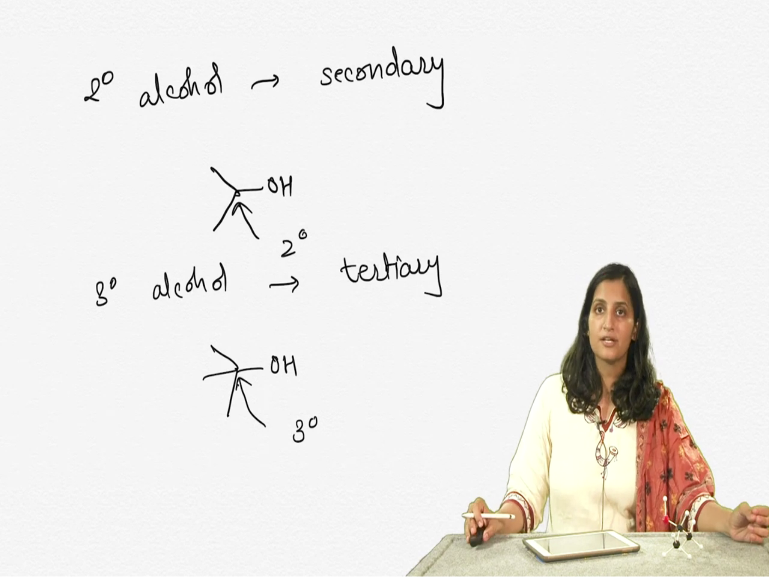

A tertiary alcohol will be such that tertiary butanol and the carbon here which is attached to the OH group is tertiary in nature; it is attached to three other alkyl groups, right. It is good to remember this nomenclature because we are going to look at reactions and you will see that primary alcohols behave a little differently than secondary and secondary behave a little differently than tertiary. And, the nature of the substitution of alkyl groups on that carbon plays a role in the whole reactivity of alcohols. So, that’s why it’s good to know this nomenclature to begin with.

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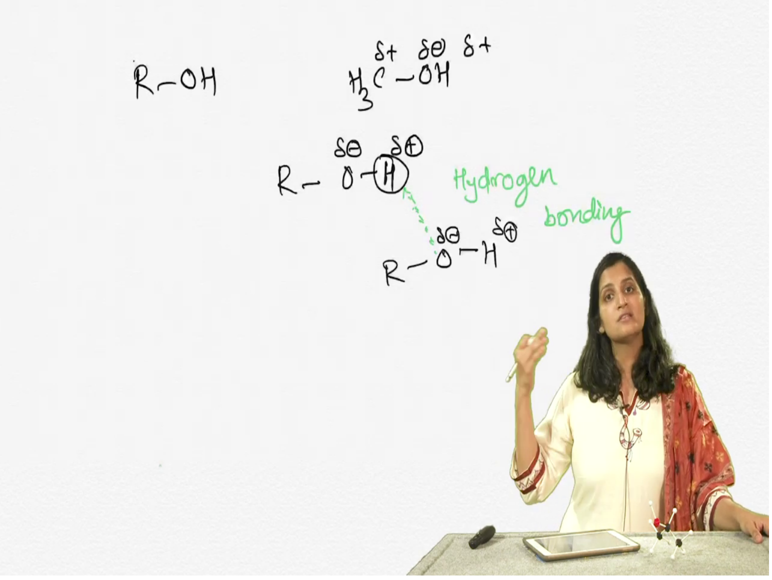

Let us look at the physical properties of alcohols a little bit. Now, alcohols are very similar to water. So, you can imagine that the physical properties of alcohols are going to be closer or at least the low molecular weight alcohols are going to be closer to that of water. And, which is kind of true in the sense that the presence of this OH group in the case of alcohols make it a very polar compound, right. And if you think about it ROH, or for example, let’s take the example of methanol, the oxygen is more electronegative, right.

So, what happens is, there is a partial positive charge on this carbon, a partial negative on that oxygen and another partial positive charge on that hydrogen. Because that oxygen is electronegative it is kind of pulling electrons from both sides really making this whole molecule a polar molecule. Now, this kind of attraction between oxygen and hydrogen where the oxygen bears a negative charge, delta negative and hydrogen bears a delta positive leads to something called as a dipole-dipole interaction because there is a dipole created between a positive and a negative end.

What we create is a dipole-dipole interaction between the two alcohol molecules, okay. Now think of it, this hydrogen is attached to something really electronegative. So, oxygen, nitrogen are the atoms that are very electronegative in nature and thus it creates a partial positive charge on that hydrogen. You take another alcohol molecule in its vicinity, that alcohol molecule will also have similar charges.

And what happens is that a partial bond of attraction is created between the hydrogen that is the positive end of one of the dipole with oxygen that is the negative end of the other dipole. And this kind of interaction is kind of strong interaction and this is named as hydrogen bonding, right. So, in the case of alcohols what you will see is that multiple molecules are attached to each other through this hydrogen bonding, right.

So, one thing to note is that this is not to be confused with the OH covalent bond, okay. The length of the hydrogen bond for example, in water is a round 117 picometers and it is kind of much-much longer 80 percent longer than the OH covalent bond, right, or the strength of hydrogen bond in water is approximately 5 kilo calories per mole.

But the strength of the OH covalent bond in water is 118 kilo calories per mole. So, it certainly weaker, much-much weaker than OH covalent bond but 5 kilo calories per mole is not a small amount. And especially if you think of multiple such hydrogen bonds existing together cumulative effect of this hydrogen bond really plays a huge role or plays a huge effect on the physical properties of water.

And, because of this hydrogen bonding the molecules are very close to each other they are attached to each other and there is an extra energy which is required to separate these molecules from their neighbors. And, that’s why the boiling point of water is 100 degrees; it’s relatively high and you need to supply energy to break this hydrogen bonding as well. And this same trait is seen for alcohols as well.

So, if you compare the compounds that have the same molecular weight or similar molecular weight. You will see that alcohols are the compounds that have higher boiling point amongst all other functional groups; that is because of the presence of hydrogen bonding between the polar OH groups. So, for example, if I take the boiling points of hexane versus 1-pentanol versus 1,4-butanediol, you can see that 1,4-butanediol which boils at 230 degrees is going to be the highest boiling as compared to 1-pentanol which boils at 138 degrees.

Whereas, hexane which does not have any OH group will boil just at 69 degrees centigrade and all of these have approximately same molecular weight. But as you can see as we go on increasing the OH groups in the molecule the number of hydrogen bonds that the molecule can form with each other also go on increasing thus increasing the boiling point of that particular compound.

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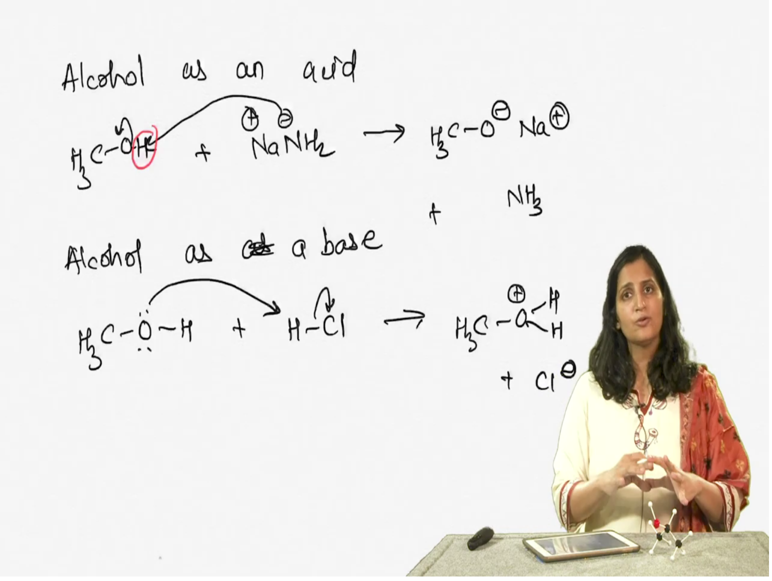

When it comes to the chemical properties of alcohols, remember that alcohols can function as both weak acids, these are the proton donors and also weak bases so, which are the proton acceptor. So, we have in fact looked at various reactions of alcohols before. And one of the reactions let's say where alcohols functioning as an acid is when let's say I react methanol with sodium amide. Then what we see is that this will easily grab this proton creating methoxide and ammonia, right.

And this is when the hydrogen here is going to be given off and the alcohol, methanol is going to act as an acid. Whereas I can also write a reaction where alcohol OH will function as a base and in this case let's take the same molecule methanol but I am going to react it with HCl. So, I am going to react it with a stronger acid; what you will see is that the OH will attack the proton of HCl and will get protonated really forming a protonated alcohol molecule and Cl^-, right.

So, alcohol that OH functionality can act as an acid also it can act as a base. Another important thing to remember when it comes to the general reactivity of alcohols is that the OH in itself is a very bad leaving group. One thing that you can really remember is OH is a very bad leaving group, it will not leave on its own in a chemical reaction.

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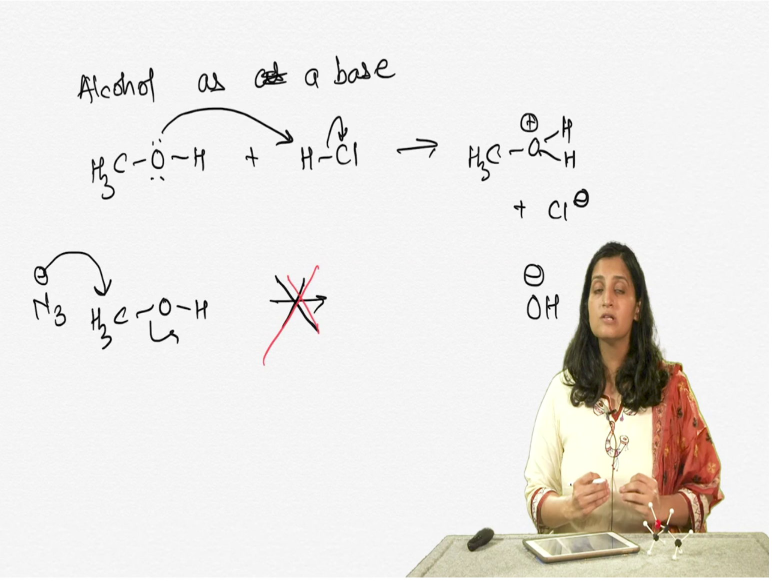

So, for example we have seen substitution reactions, right, something like S_N2 reaction. Let's take methanol the same molecule and let's attack this carbon with a good nucleophile like azide. Now what one could expect is that the azide could attack here and kickoff this leaving group, but this really does not happen because if it were to happen you would be creating a hydroxide ion. Now hydroxide ion on its own is really unstable right; if you want to think about it, hydroxide is a really strong base.

So, its conjugate acid water has a pKa close to 16; thus making it a very bad leaving group. And so, in most chemical reactions of alcohols we cannot kickoff that hydroxide ion as a leaving group. So, alcohols for example, will not do S_N1 or S_N2 reaction. Where the OH is or OH^- is kicked off as a leaving group. Now there are some exceptions to this rule, but more often this can be remembered as a general rule that OH is a very bad leaving group, okay.

So, if I have to summarize the reactivity of alcohols, when we have to predict the mechanisms of reactions that have hydroxyl groups. One thing we need to remember is that these are both weak acids as well as weak bases. So, you could add a proton on that OH or you could take a proton away and these could be one of the most initial steps of the mechanism when you have a strong acid or a strong base present in the reaction.

The other thing to remember for reactivity of alcohols is that because the OH is a very bad leaving group. One of the main steps in the mechanism is to first convert it into a good leaving group and then make it leave. So, you will see reactions where the OH which is a very bad or poor leaving group reacts with protons or reacts with a strong acid to create something like OH_2^+ which is water.

And water is a good leaving group and thus you will see reactions where OH is converted to OH_2^+ by reacting with an electrophile. Or you will also see converting OH to something else like converting OH to bromide, converting OH to a chloride. Thus enabling the subsequent chemical reaction which is a substitution reaction. Okay so, these are the two main things that you want to remember when your thinking about alcohols and their chemical reactivity.

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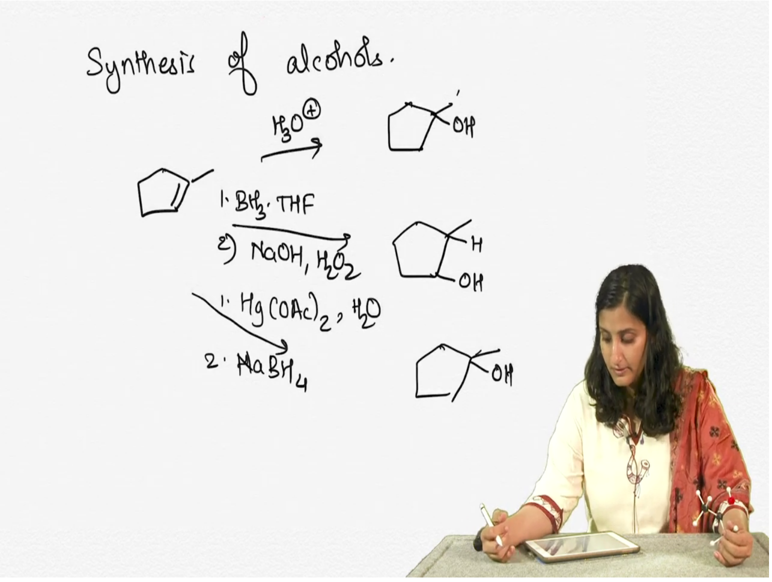

Before we go ahead with the reactions of alcohols let us remember the ways we have seen to create an alcohol molecule. So, for example, we have seen reactions of alkenes, right and we have seen reactions of alkenes, where alkene when reacted with in an electrophilic addition reaction like with H_3O^+ you can form the addition of OH and H across that carbon-carbon double bond such that the OH goes to the more substituted carbon. Or we have also seen reactions like hydroboration-oxidation wherein that OH ends up on the less substituted carbon of the carbon-carbon double bond.

We have also seen one more reaction which is the reaction of oxymercuration and reduction right, which will also place the OH on the more substituted carbon. The difference between oxymercuration and reduction versus the reaction with hydronium ion is that, in the case of hydronium ion there is the formation of carbocation and you can have carbocation rearrangement. But for example, in the case of oxymercuration you will get the product without rearrangement of the carbocation.

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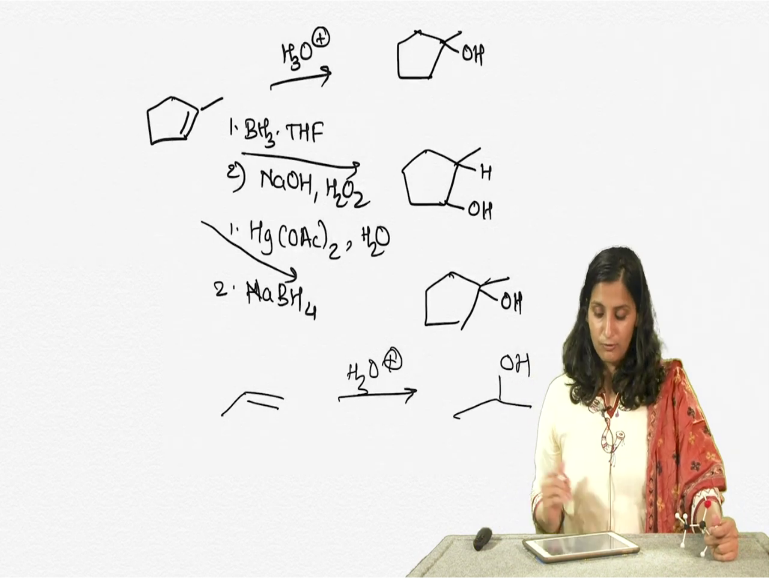

So, hydration reaction of alkenes is very often used to form alcohols. And, in fact the isopropanol molecule that we have seen is made globally, around 2 million tons of isopropanol is used globally every year. In which the isopropanol is created via hydration of propene. So, you could take propene and with H_3O^+ it is going to form this isopropanol molecule. So, this is an industrial preparation and it's used widely across the medicinal fields as an disinfecting agent due to its low toxicity, right. So, we have seen these reactions when alkenes react to form alcohols.

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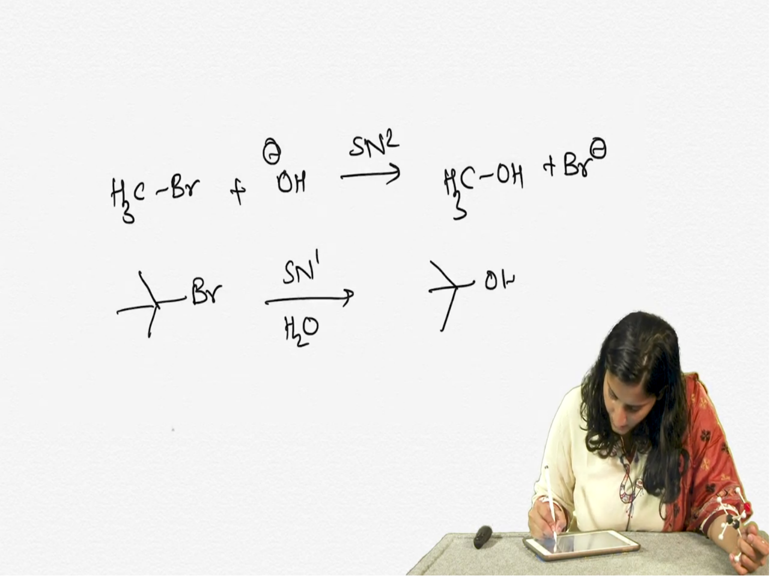

We have also seen the reactions from alkyl halides, when you can use a primary alkyl halide and do S_N2 reaction to form an alcohol. So, for example, I can react methyl bromide or let's say ethyl bromide with hydroxide as a nucleophile and create methanol. So, you can do S_N2 chemistry on a primary or a methyl carbon. Sometimes even on a secondary carbon to form the corresponding alcohol. So, hydroxide would be the nucleophile in this case.

Or we have also seen when a tertiary alkyl halide will react with water for example, to give you a tertiary alcohol. So, I can take tertiary butyl bromide and react it in an S_N1 reaction let's say with water and this will give rise to tertiary butanol. So, we have really seen these many reactions to convert either alkenes to alcohols or to convert alkyl halides to alcohols. Now, you may also remember the reactions which we have seen to convert alkenes to alkyl halides.

So, I am not covering these, but you may want to think of how to convert the functional group of alkenes to alkyl halide and an alkyl halides to alcohol. So, this is how chemists think of synthetic schemes to go from one functional group to another. Anyway, so these are the reactions we have seen to make alcohols. Now when alcohols react they are going to react in various different ways and let's now look at the reactions of alcohols.

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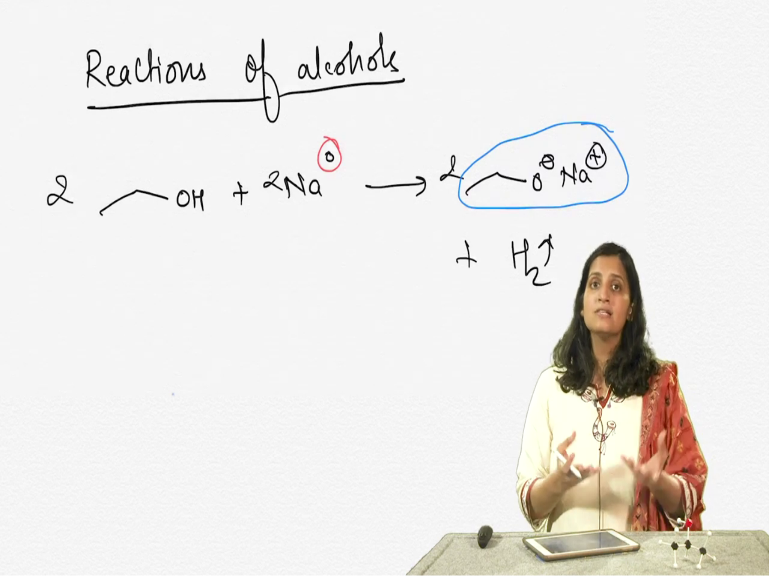

One of the iconic reactions of alcohols, which is used as a deterministic test of an alcohol is when alcohols react with the elements from the first group which is lithium, sodium, potassium or other active metals really to liberate hydrogen, okay. So, when alcohols react with sodium for example, they will form hydrogen and the corresponding metal oxide, okay.

This is kind of an oxidation-reduction reaction. So, sodium will get oxidize to Na$^+$ and H$^+$ which is formed in this reaction is reduced to form hydrogen gas H_2. In fact, you might have done this reaction as a test of alcohol. So, if you take a test tube, you take an alcohol in it and add sodium to it, the gas that comes out of the test tube you can hold a flame to it. And you will hear a puff sound which indicates that hydrogen gas was liberated, is one of the more known tests of identifying alcohol as a functional group, okay.

And let's look at this reaction, let's take ethanol and let's put sodium metal, now this 0 on top here for example, is used to indicate the metallic state of sodium. And what we form here is sodium ethoxide and hydrogen gas. And this hydrogen gas as I said can be tested to confirm the presence of an alcohol. If you really think about it the alkoxide that is formed is kind of useful in many other chemical reactions.

So, alkoxide ions are nearly the same or even stronger bases than hydroxide ions and that's why these alkoxide ions can be used as bases in organic reactions that require a strong base. Like for example, in an E2 reaction and which requires a non-aqueous solvents. For example, alcohol is a non-aqueous solvent and you can use sodium ethoxide in ethanol as a base to work in an E2 kind of reaction.

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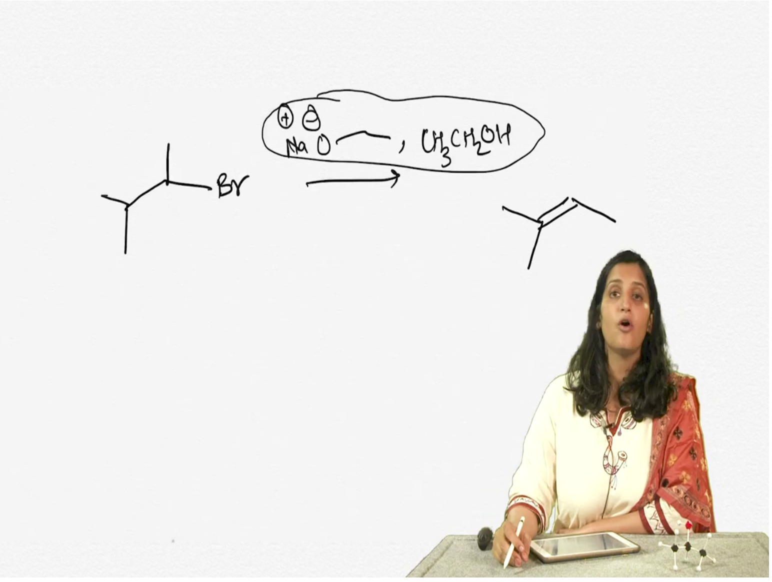

So, just to remind you we have seen E2 reactions like these, wherein sodium ethoxide and ethanol can be used as a reagent to perform the E2 chemistry and to work as a base to form the final alkene.

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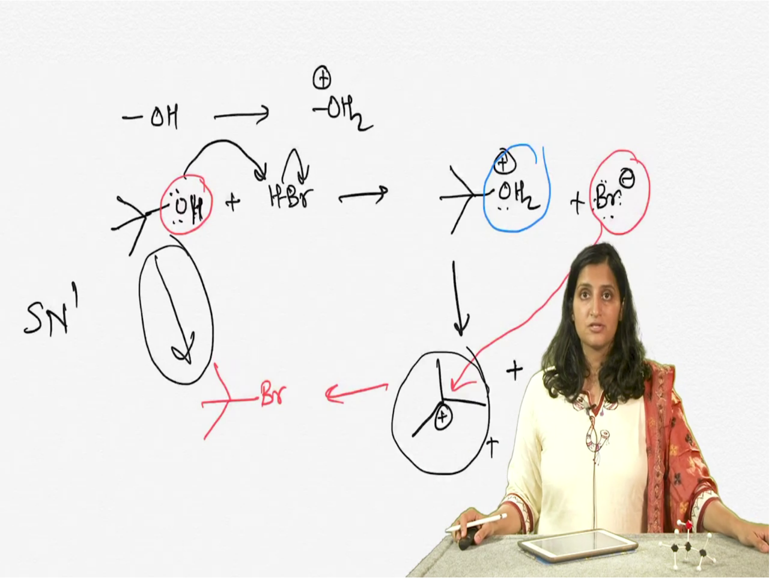

As I said before most of the reactions of alcohols will involve a step wherein the bad leaving group OH is converted into a good leaving group, okay. Now, we are going to look at a couple of reactions wherein we first convert this bad leaving group of alcohols to a good leaving group. The first strategy of converting OH into a good leaving group is conversion from OH to OH_2^+, right.

So, let's look at how to convert a tertiary alcohol into a good leaving group using this strategy. So, tertiary alcohol for example, I am going to take tertiary butanol, when you react it with a really strong acid like HBr remember alcohols because they are weak bases as well. The first step happens wherein the OH will attack this proton and form this protonated alcohol molecule.

Now, suddenly from this OH which was a bad leaving group, we have converted a good leaving group which is water. If you think about it, the reason why OH is a bad leaving group because it leaves like a hydroxide ion and it is charged; 'nature hate charges'. Whereas, water when it leaves, this OH_2^+ as it leaves it's going to leave as a neutral water molecule and it's going to be a stable leaving group. And so, in the first step when you form this protonated alcohol and for example, a bromide ion in this case, you have converted the OH which was a bad leaving group into a really good leaving group which is water.

Now, in this case what happens next is that since you have a good leaving group, it's going to leave creating water and tertiary butyl cation, right. Once we have created this, remember the bromide that escaped in the first step it can attack on that cation to form tertiary butyl bromide and water has escaped as a leaving group, okay. So, tertiary alcohols can react rapidly with HCl, HBr, HI. In fact, you can take any alcohol, water soluble tertiary alcohol, and you can mix it with a concentrated acid for a few minutes at room temperature it will result into the corresponding alcohol to the haloalkane formation, right.

So, we have converted the tertiary butanol to this tertiary butyl bromide. And this conversion is possible really at room temperature as well. So, if I really ask you what was this whole mechanism like? So, this is a S_N1 mechanism, right; you first form the good leaving group, the good leaving group left forming a carbocation and that carbocation was later attacked with something else that substituted the position of the starting alcohol, right.

So, this is substitution nucleophilic unimolecular reaction. And this is possible for a tertiary alcohol the reason is that the carbocation that we are creating in one of the steps is stable enough, right. So, tertiary alcohols can be converted to corresponding haloalkanes using S_N1 type of chemistry; the same does not really work for primary alcohols. So, now, let us look at one of the reactions of primary alcohols and how primary alcohols react with HCl to do the same kind of chemistry.

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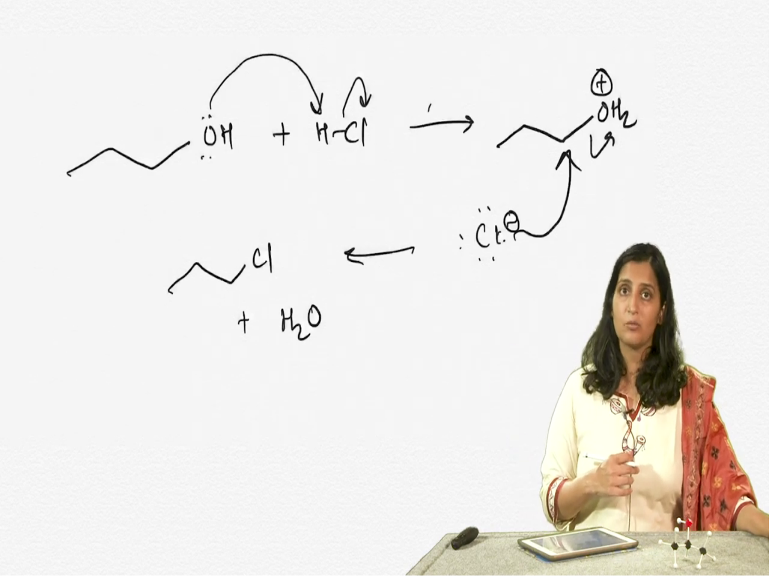

So, now I have propanol here and let’s take propanol and react it with HCl. The first step of course, is such that the OH will attack the proton of this HCl and it will act as a base really creating a good leaving group on that oxygen. Although, we have created a good leaving group remember that if it leaves you are going to create something unstable because the primary carbocation that will be created will not be stable enough, right.

So, there is no driving force for this protonated alcohol molecule to react in an S_N1 fashion, right. This oxonium ion is thus not going to take part in S_N1 chemistry. Instead what will happen is that the chloride ion that escaped will come back and attack this carbon and kick out the leaving group, okay. So, this is more like an S_N2 type of chemistry and what you will create here will be the chloride and water molecule that leaves as a good leaving group.

So, we have seen how tertiary alcohols react in S_N1 fashion with HBr; the same reagent HBr will react with primary or methyl alcohols as in an S_N2 fashion. Now, for secondary alcohols it really depends what kind of molecule the secondary alcohol is and it may go via $S_N1$or S_N2 chemistry depending on the stability of that particular carbocation.