Introductory Organic Chemistry
Dr. Neeraja Dashaputre
Department of Chemistry
Indian Institute of Science Education and Research, Pune

Lecture - 50
Ethers and Epoxides Part-2

If we have to talk about reactions of epoxides as I said previously, one of the key reactions of epoxide is the ring opening reaction.

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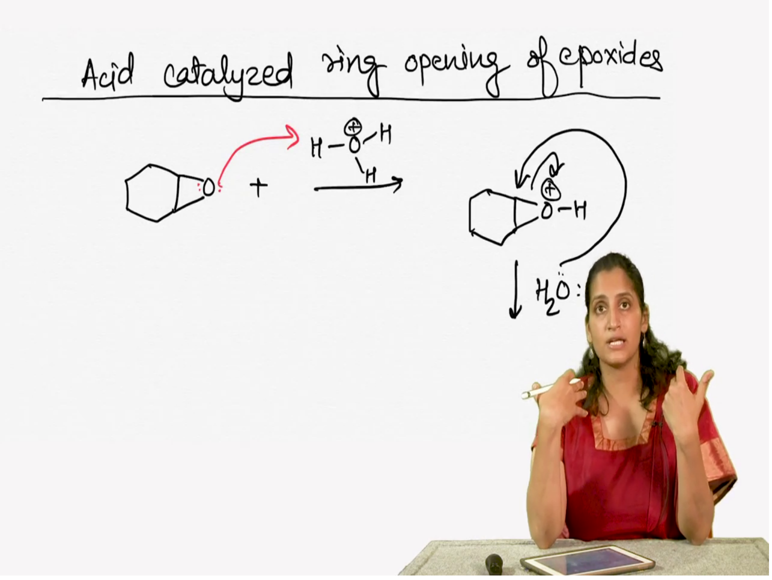

So, now let us look at the first reaction of epoxide wherein we talk about acid catalysed ring opening, okay. And we are going to begin talking about this reaction by taking an epoxide and we are going to put it in dilute acid, so let's say something like H_3O^+, okay. Now, the first step of course, will be such that the lone pair of this oxygen is going to get protonated.

So, whenever you have an oxygen in the molecule for most functional groups like alcohols, like ethers, like epoxides or carbonyl functional groups. And when we put it in an acid one of the first step that really happens in any reaction mechanism is that oxygen will get protonated.

Now, in presence of acid catalyst what happens is, it's going to get protonated. Now, if you think about it what happens next is a water molecule will come and will attack this carbon to kick open this particular three membered ring. Now, why is this kind of step very acceptable?

First of all because you are trying to release the strain that is present in the ring and attack of water is facilitated by the fact that the formation of a less strained molecule takes place at the end of the reaction.

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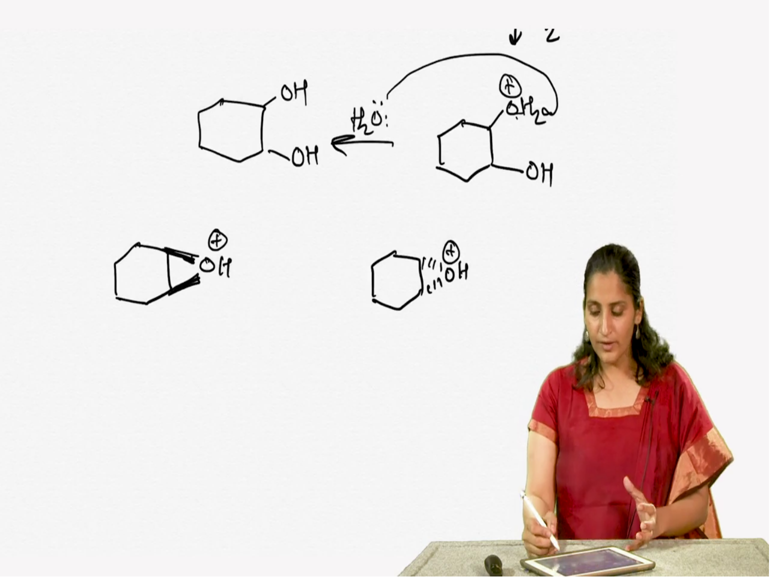

So, what happens in this step is formation of unprotonated glycol, okay, and in fact, in the next step another water molecule will come and deprotonate that particular protonated water to give you a glycol. Now, if you think about it I have not really shown the geometry in this case, but any epoxide especially on a ring will be form such that either this epoxide ring is coming towards you or it is going away from you, right.

So, there are two ways to represent this epoxide, either I can draw the epoxide like this or I can draw an epoxide that looks like this, right, and what happens is when it gets protonated it's going to look like this. So, in the first step when the oxygen attacks a proton we have really created these two compounds.

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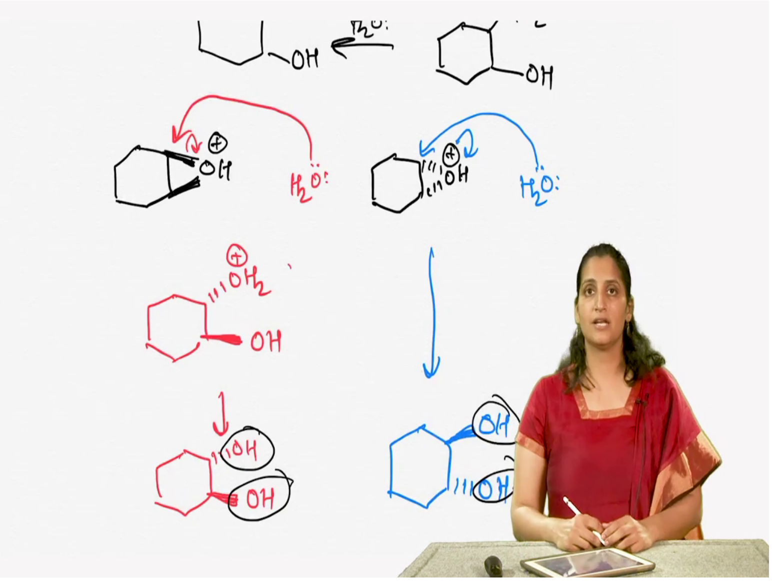

Now, when the incoming water has to attack; remember just like in the case of bromonium ion since the ring is forming towards you, kind of like this, the incoming water has to come from the backside, right. It cannot come from the front because this oxygen is kind of creating a steric hindrance for the attack.

And so the incoming water molecule in the first case will come from the back and will form a product in which this OH bond is at the back whereas, this OH bond did not take part in this step so it remains the same, really resulting into the product that looks like this. Whereas, if the water was going to attack this other epoxide it would attack it such that it would attack it from the front and resulting into the formation of this compound, right. So, the main thing to remember here is that the two OH’s that we have formed are such that they are going in opposite directions, so this results into the formation of trans diols.

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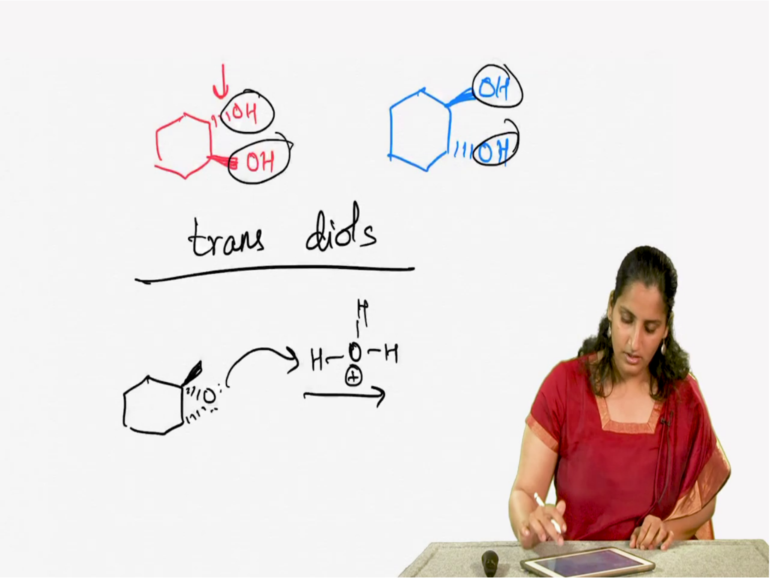

We have previously seen a reaction wherein syn diols are formed that was the reaction of alkenes with OsO_4. But the acid catalyzed opening of an epoxide really results into the formation of trans diols wherein the two OH groups are going opposite to that of each other. And that is because the reaction mechanism is very similar to the formation of that cyclic bromonium ion that we had seen.

If we want to dwell into this reaction further let us take an asymmetric epoxide, okay; we are going to start with this molecule and let's say now we want to put it in an acid, right. The first step of course, would be such that it results into the protonation.

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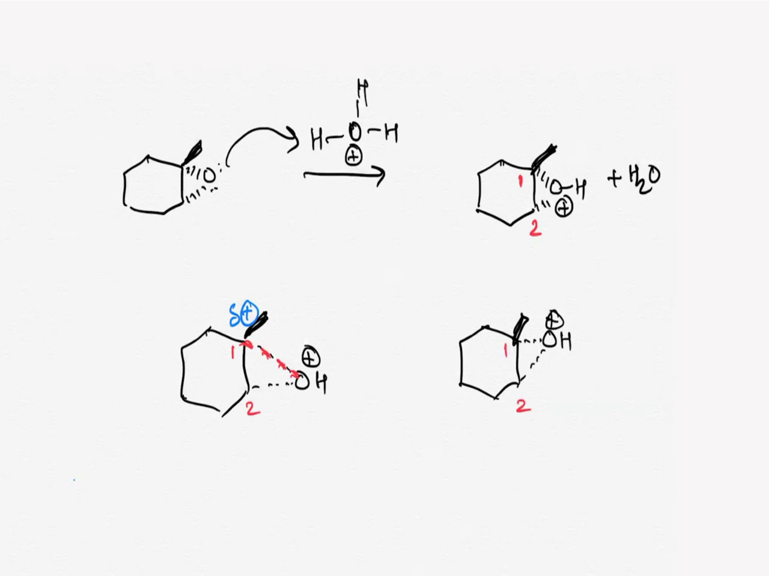

Now, if we have to ask which one of these two carbons would this water prefer attacking. We have carbon number 1 which is more substituted, and we have carbon number 2 which is less substituted. To think about it may seem logical for the water to attack the less substituted carbon, right because it is less substituted, there is less steric hindrance.

But if we think very carefully about it what you will realize is that this is quite similar to the bromonium ion formation, right. And when we talked about bromonium ion we talked about the carbocation character that gets developed in the transition state, right. So, something similar is going to happen here what it means is that oxygen is not gonna be held equally and such that the oxygen is kind of making both the bonds equally with the two carbons.

In fact, it’s gonna be swaying around and because bonds are nothing but electrons right, although we show it with a ball and stick model bonds are nothing but electrons. And the oxygen thus is not shared equally between the two carbon such that it is not always equidistant from the two carbons. And in fact, we may arrive with a situation that looks like this where in it is closer to carbon number 2 than carbon number 1 or I may also have it sometimes closer to carbon number 1 than carbon number 2.

And both of these situations are possible; however, the situation that is much more likely is the one where it is further away from carbon number 1, right. Why is that? Because as it moves away from carbon number 1 the electrons of oxygen are moving away from carbon number 1 and what starts developing is this partial positive charge on carbon number 1.

And because carbon number 1 is more substituted it can stabilize that partial positive charge better. So, between these two situations it is much more likely that the first situation happens more often wherein the oxygen is further away from carbon number 1. And as a result of which the attack more often is seen such that it happens on the more substituted carbon.

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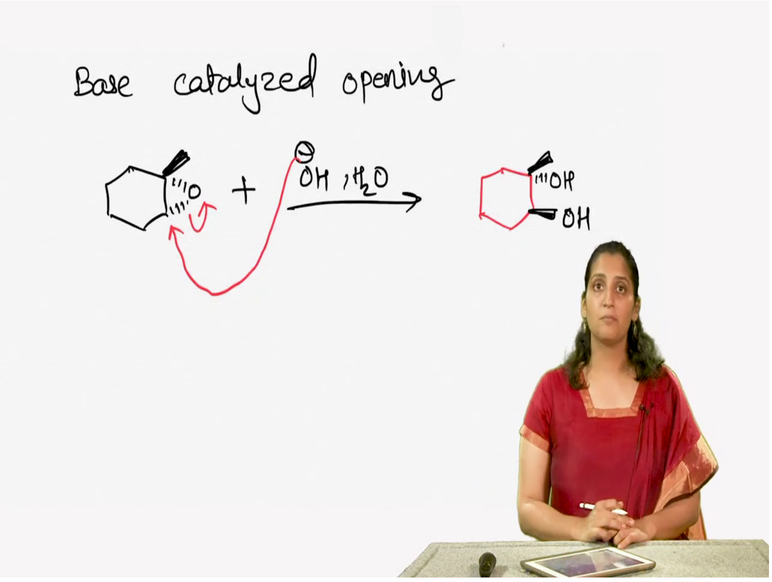

Just to give you a particular example if we start with an epoxide that looks like this and if instead of water if I am putting it in methanol and HCl. Then the final product almost always is such that we see the methanol ending up on the carbon number 1 or the top carbon in this case. And it results into the formation of this molecule, right; this molecule is seen as the major product, right wherein the OCH_3 is seen attached to the carbon that had more substitution on it.

Now let us look at the opposite of it which is the base catalyzed opening; if you think about it, in acid catalyzed opening we started with H_3O^+, in base catalyzed opening we can start with NaOH solution. In the case of base catalyzed opening since we are in presence of base, protonation is of course, not the first step of the reaction. And the base here OH^- being a very good nucleophile can attack on the carbon and kick open the epoxide ring. What is important is that in this case we have to pay attention to the fact that the protonation has not happened, so that oxygen atom is kind of held equally between the two carbons.

The kind of situations that we talked about previously for acid catalyzed opening wherein the oxygen was kind of swaying away. It was possible because the oxygen was protonated; it had hydrogen attached to it and it was possible for that oxygen to move around like that. But in the case of base catalyzed opening since that oxygen is not protonated the first step that happens is that the OH^- will attack the less substituted carbon. And why the less substituted carbon in this case? Because the oxygen of OH^- is going to prefer an attack where there is less steric hindrance and as a result of which the product that forms is this, right.

So, in the case of acid catalyzed opening we are attacking on the more substituted carbon whereas, in the case of base catalyzed opening the attack happens on the less substituted carbon. And just to revise both of these acid and base catalyzed openings really result into the trans diols whereas, the reaction of OsO_4 and peroxide that we had seen results into the formation of syn diol.

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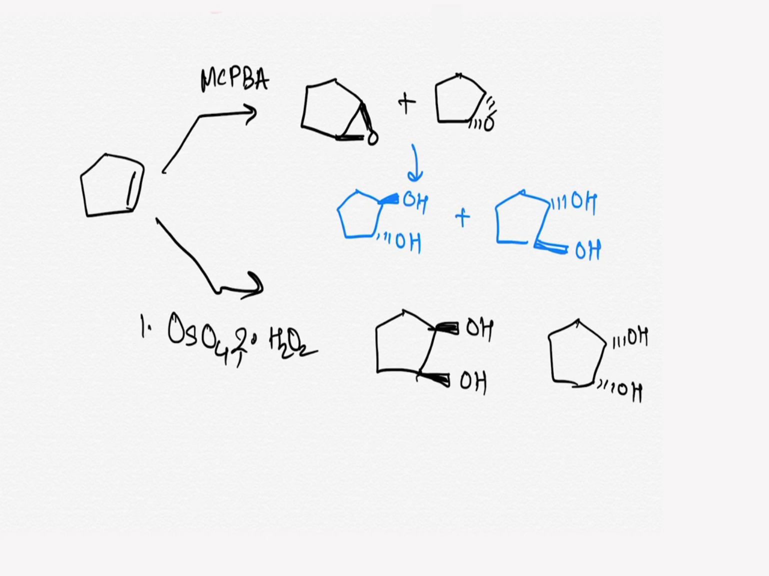

So, if I start with an alkene and let's say the first step is MCPBA, it will form the corresponding epoxide, right. When this epoxide opens up in the case of acid or base catalyzed opening it's going to form the trans diol and this is nothing but a racemic mixture of two, so we will form a racemic mixture, but it will not be optically active. In the second case if we start with OsO_4 as the first step and second step as H_2O_2 then what we really see is this formation of syn diols and this is an achiral molecule because it has a plane of symmetry.

So, depending on the method of preparation of diol we can actually form trans or syn diol depending on how we do the synthesis. Epoxides are really very important building blocks in the case of organic synthesis because what happens is that epoxides are so reactive, they can be easily converted through various other functional groups. You just need a good nucleophile to kick open an epoxide and it opens up to form a whole new molecule which also has an alcohol end to it and that alcohol can further be converted to various other functional groups.

So, that’s why epoxides are one of the main building blocks when it comes to synthesizing various organic compounds. So, that was it for the reactions of epoxides and for that matter for this chapter of alcohol, ethers, thiols and epoxides. We have looked at alcohols in depth but we have also looked at these other compounds or these other functional groups and we have started understanding their chemistry a little bit.