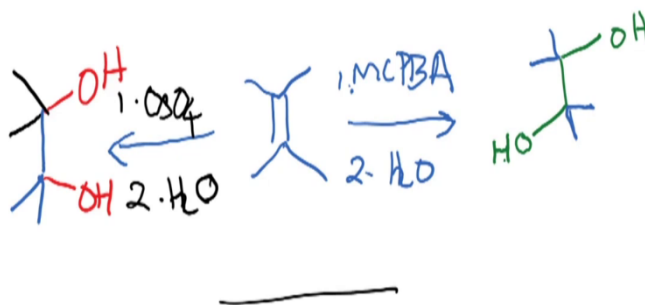**Introductory Organic Chemistry II**
Professor Doctor Harinath Chakrapani
Indian Institute of Science Education and Research, Pune
Module 08
Lecture 59
**Named Reactions - Part 2**

(Refer Slide Time: 00:16)

So, in the previous lecture, we were trying to add dihydroxyl groups to an olefin. So here is the olefin. And so, you have two major methods by which you can add two hydroxyl groups to an olefin. So, one is the MCPBA method. So, where you do first make an epoxide followed by hydrolysis, and the epoxide, once it undergoes hydrolysis, it is going to give you the anti-alcohol, so you are going to get OH and OH.

And so, this is a very good way to make anti-alcohols. Now, the second method is to actually to do a osmium tetroxide reaction followed by hydrolysis again. Now, of course, we also discussed that you can use the N-methyl morpholine oxide, and this is going to give you the syn alcohol. So, you have this and this and here are your two functional groups.

So, these are two important methods by which you can do Bis-hydroxylation, so with that, what we will do is we will look at two additional methods to do Bis-hydroxylation.

(Refer Slide Time: 01:43)
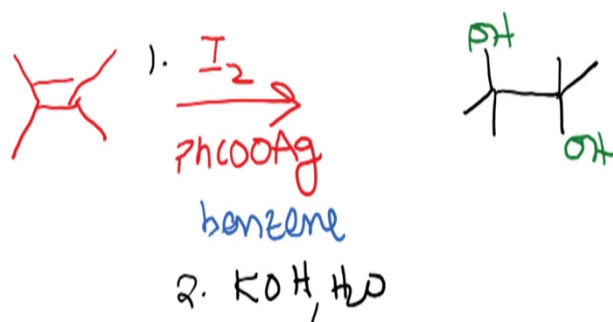
They are very very interesting from a mechanistic standpoint and the reagents are very simple. So, you start with an olefin and you add iodine in the presence of PhCOOAg which is silver benzoate and you usually add benzene as a solvent. So, under these conditions, you end up getting a diol and we will work out the stereochemistry of the diol, but the second step here would be you need to add a base and water.

And you end up getting a diol which is actually anti-diol. So, you get OH and OH. So, now, let us go to the next slide and try and work out the mechanism.

(Refer Slide Time: 02:46)
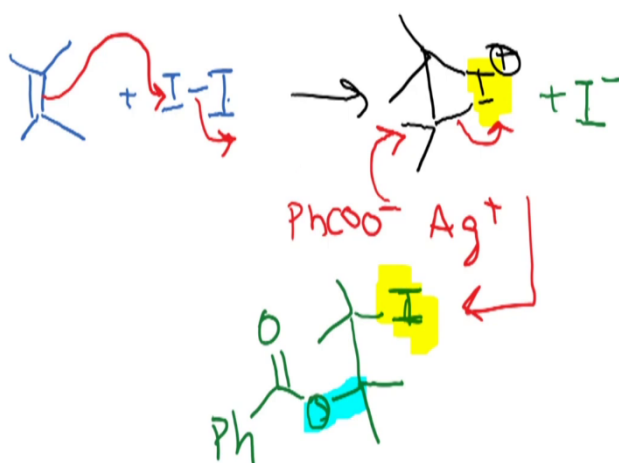
So, when we start with the olefin, in the presence of I_2, so, iodine acts pretty much like how bromine does, I think we all know that. So, if I have to push an arrow from the olefin, so then I will attack the I iodine and then this is kicked out and what we get as the product would be the cyclic iodonium ion, and iodide as the byproduct.

So, this first step is fairly straightforward. Now, you have several possibilities for this iodonium ion. One is that if I^- is the only nucleophile present I^- can attack and give you the diiodide. But we already told you that there is benzoate that is present. So, benzoate, now, this $PhCOO^-$ can actually attack over here and open up the cyclic iodonium ion and you end up getting the following product.

So, this is $(CH_3)_2(I)CC(CH_3)_2OC=OPh$. So, just to be clear, so this iodine is the cyclic Iodonium ion. And this is the I that is present it is I^+ and it becomes a neutral iodine. And here is the new bond that is formed between carbon and oxygen. Now, please keep in mind that the relative orientation over here is basically anti, that is the oxygen is now going to be in the opposite side of the iodine.

(Refer Slide Time: 04:42)
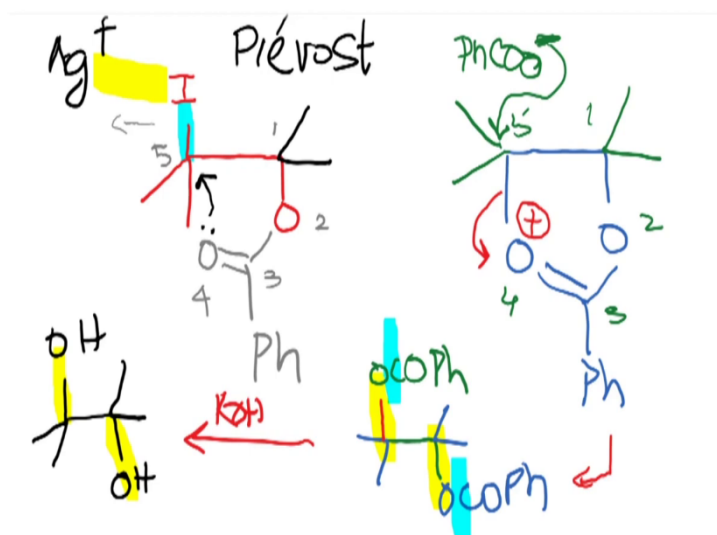
Now I am just going to redraw this in the next slide so that we have some space to work out the mechanism. So, the way I am going to draw it is the following. So, I draw Iodine, this group is over here. And you remember that OCOPh is there and then you have the other two groups. Now if you remember there is a Ag^+ that is floating around in the solution.

And so, this is going to start coordinating with iodine and many of you know that silver really likes halogens. And so, once silver forms a strong bond with halogens, then you are going to form a solid which is going to precipitate. So, I am going to do one thing here is that I am just going to draw this OCOPh in a little different way, so that we can understand the reaction mechanism better.

So OCO, I am going to draw it this way, with the Ph, and so keep in mind that the electrons are being pulled from iodine or are being pulled towards silver, and that is going to make this bond quite weak. And what happens is that this lone pair, which is present here, actually ends up attacking this iodine, and you get the following product. So, I am just going to number this so that it is easy for us to follow.

So, this is number 1, 2, 3, 4, 5, so you get a 5-membered ring which is formed. So, you have O O Ph, this double bond remains the way it is. So just to complete the numbering, this is over here 1, 2, 3, 4, 5 and you still have a positive charge over here. So, this is going to be the important intermediate that is formed. And this intermediate sort of allows for us to understand the stereochemistry here.

So, since this oxocarbenium ion is present on one side, the incoming nucleophile, which is PhCOO$^-$, attacks from the opposite side, and so when it attacks here, you end up breaking this bond, and the resulting product is actually anti. So, I am just going to draw out the structure over here, so that you guys understand stereochemical aspect of it clearly.

So, just going to little bit make some space so that it is easy for us to follow. So, your new benzoyl group is over here OCOPh and the old benzoyl group continues to be here OCOPh, the only thing here is that they both are anti to one another. So, this is the important intermediate that is formed.

So, the relationship between this bond and this bond is actually anti and the relative stereochemistry is going to be anti and so, the next step, when you add KOH, this results in the hydrolysis of the ester, which is over here, and it gives you the diol, which is anti-diol. We will look through this a little bit during the problem-solving session, but this kind of

molecule, this kind of reaction condition actually is very interesting and it exclusively gives you the anti-product.

So, this reaction has a name, the name is not very important to us, but the reason why the name reaction is important is because it is an important reaction and therefore it has a name. So, this is called the Prevost reaction and now there is a, an accent on the e. So, this is Prevost reaction, I might be pronouncing it incorrectly, but this is the reaction that was developed by him. So, in the next, we will look at a modified version of this and that's called the Woodward reaction.

(Refer Slide Time: 09:19)
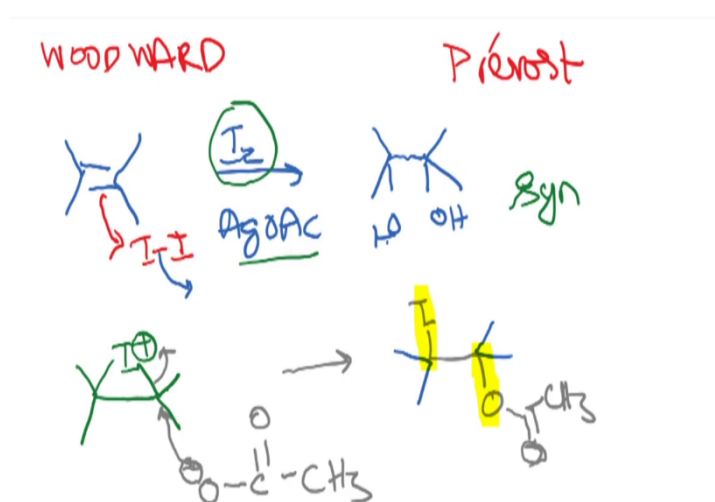
So, we were looking at possibility of dihydroxylation reaction with silver benzoate and iodine and so on. So, very famous organic chemist Woodward came up with a modification of the Prevost reaction and so the modification he made was the following. So, he took an olefin and instead of silver benzoate he added iodine and silver acetate.

And, this is followed by hydrolysis reaction, but the important difference here is the silver acetate that was used. And he actually ended up getting the alcohol which is syn diol. So, this is called as the Woodward modification to the Prevost reaction or also called as the Woodward reaction.

So, when you use iodine in the presence of silver acetate, the product followed by subsequent hydrolysis, the product that you get is actually syn-diol. Now, let us look at the mechanism,

the mechanism has very similar features to the Prevost reaction. So, for example, reaction with iodine remains the same. So, when it reacts with iodine, you kick out iodide, and it gives you the cyclic iodonium ion.

And the remaining sort of geometry of the double bond remains the same. Now, instead of benzoate, we have an acetate, so acetate now has to approach from the backside, as all of you know, so it is going to attack from the back, and it opens up this iodide over here or the carbon-iodine bond is broken. And the product that is formed is $I(CH_3)_2CC(CH_3)_2$ $OC=OCH_3$, and the rest of the molecule remains the same. So now if you see the relative geometry, or the orientation of these two is actually anti.

(Refer Slide Time: 11:47)
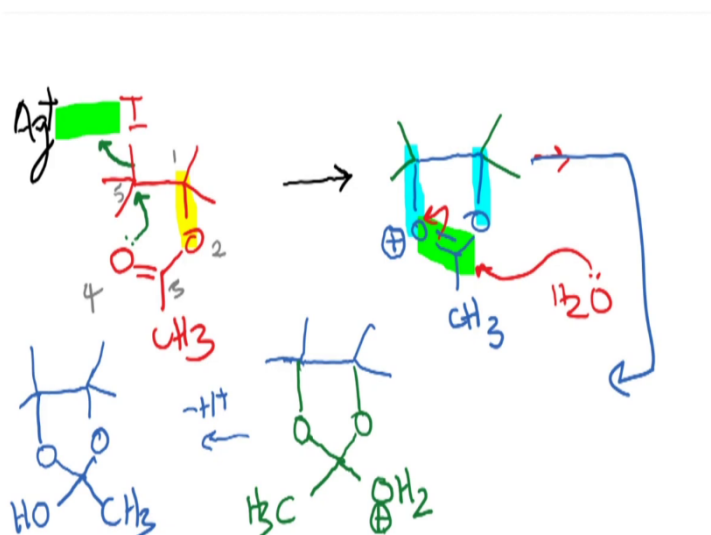
Now, I am just going to redraw this in the next slide, so that we get some more space to work on the mechanism. So, you have iodine. And let me just get this out of the way so that I can make some space on the left. So, we have iodine, and then you have O C double bond O CH_3. And the rest of the groups are the same.

Now, we propose a similar interaction with Ag^+. So, you have an interaction with Ag^+ which is going on here. And then you have the carbon-iodine bond being broken. And you can also propose that this lone pair very similarly to the Prevost reaction can attack here. So, the product that is formed is I am going to try and make sure that this is clear. So, this oxygen and this carbon are actually anti to one another.

So now, we will end up with a very similar ring size 1, 2, 3, 4, 5. So you form a 5-membered ring. So, I am just going to draw out the 5-membered ring here, so that it is easy for us to understand. And there is a CH_3 here. And this double bond remains the same, and then you get a positive charge. And rest of the molecule is the same. So now what we have done is, we have now converted an anti into a syn-diol.

So here, it is very interesting, because when this is carried out in the presence of water, so water is actually it is not a bad nucleophile it is now it can come in and attack here. And so, water actually prefers to attack over here, and this is an activated carbonyl, as you can imagine, and the product that is formed is actually an ortho ester. So, I am just going to draw out the ortho ester here, separately, so that we all understand what an ortho ester is.

So, dimethyl groups or the dialkyl groups are the same. Now, I am drawing the 5-membered ring. So, let me just get this little bit clearer, so here is the oxygen, carbon, oxygen, carbon, this is a methyl group here. And instead of now the positive charge we have OH_2^+. And so, this carbonyl carbon was actually opened up and it is quite reactive.

It reacts with water to give you this kind of a protonated ortho ester, which can subsequently lose the proton to give you an actual ortho ester. Ortho ester is an equivalent of a carboxylic acid. So, you have carbon attached to three oxygens and so loss of protons will give you this kind of an intermediate. So, this is the important difference between the two reactions.

So, that is the Prevost reaction when you generate this intermediate, this 5-membered ring intermediate, benzoate subsequently attacks and forms an anti-configuration which then the subsequent hydrolysis gives you the product but here in this case water actually attacks the activated carbonyl to give you an ortho ester which is syn.

(Refer Slide Time: 15:52)
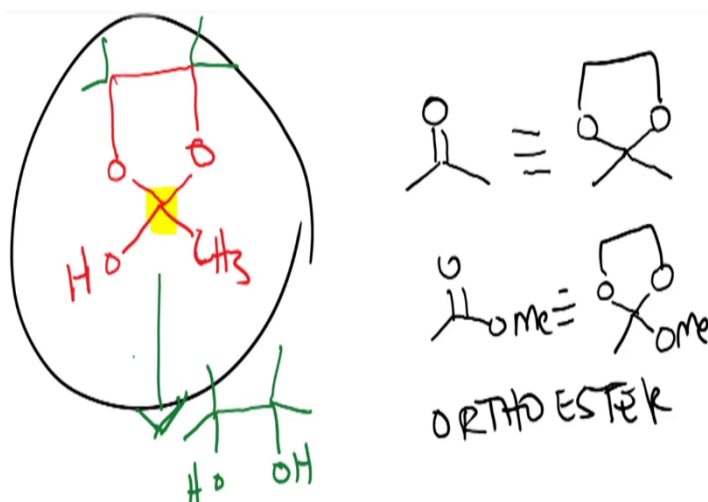
Now, let me just redraw this ortho ester so that we can understand the functional group a little better. So, if you see here this is a CH_3 and there is a carbon, this carbon is flanked by three oxygens. So, if you formally look at it, if I take a ketone, which we will study very shortly and if I react it with a diol, then I get an acetal.

Now, a similar exercise with a carboxylic acid ester will give you O O OMe CH_3. So, this is called as an ortho ester. So, this molecule over here is an equivalent of an ortho ester. You can now hydrolyze off this ortho easter to give you the desired product, which is the diol and as I mentioned earlier, these groups all remain the same, so you are going to get a syn-diol.

So, you can now go back and work out the mechanism of hydrolysis of the ortho ester and that will be something that we can look at later. But this hydrolysis is going to occur and give you the product. So just to recap the important difference between the Woodward modification and the Prevost reaction is that in both cases, we use iodine and a silver salt and in the Woodward reaction, we use an acetate and the acetate is actually going to form an ortho ester which then hydrolyze off to give you the syn-diol.