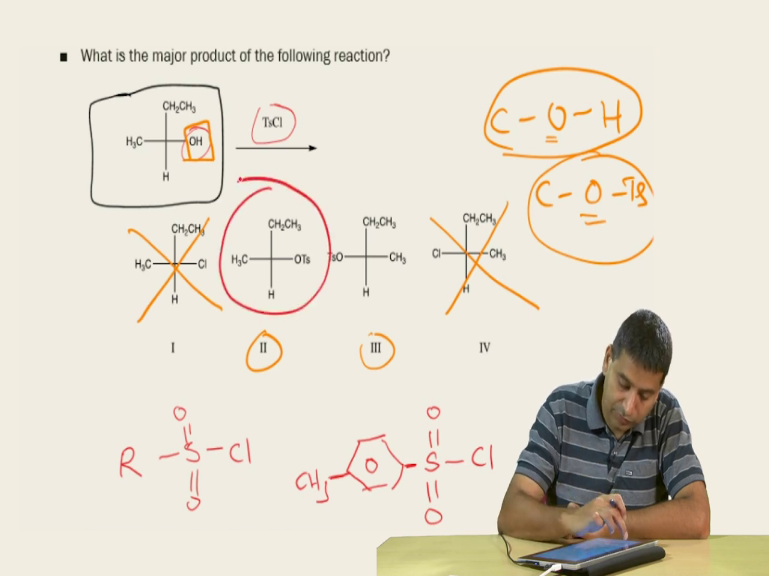
Introductory Organic Chemistry

Dr. Neeraja Dashaputre
Prof. Harinath Chakrapani
Department of Chemistry
Indian Institute of Science Education and Research, Pune

Lecture - 52
Tutorial - 08

So, welcome back to the organic tutorials; this is the last tutorials for you. So, today we look at some interesting problems that relate to the past week, okay. So, let's get started.

(Refer Slide Time: 00:28)

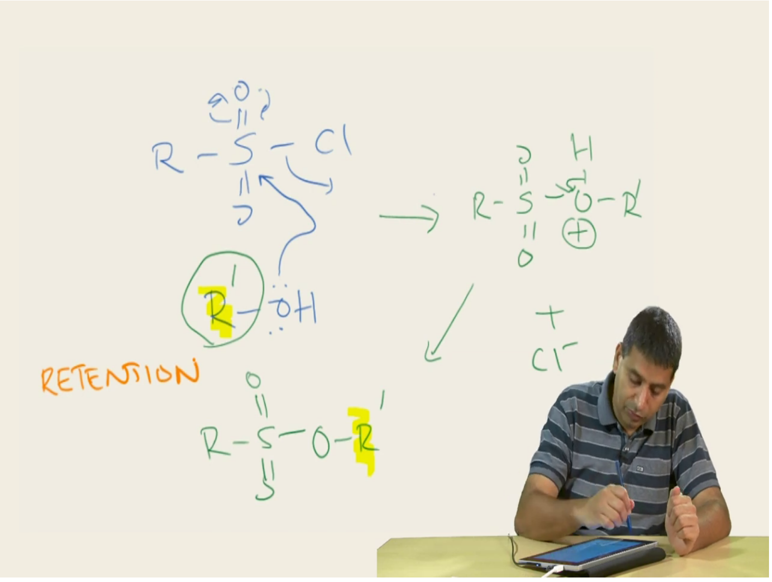


- What is the major product of the following reaction?

The first problem is what are the major product of the following reaction? So, you have an alcohol that is reacting with Tosylchloride. So, here there are two parts to this question; so first part you should know what the reaction is about that is how does an alcohol react with this sulfonyl chloride? Just to remind all of you sulfonyl chloride is nothing, but S double bond O, double bond O, Cl and you can have any R group here and in this particular case the R group is para-toluene, that means that, CH_3.

So, please remember that the bond is between a carbon and carbon not between carbon-hydrogen, but it is represented in this following way. So, you have S double bond O, double bond O, Cl. So, this is the tosylchloride and it is supposed to react with an alcohol. So, the first thing in this question is how does an alcohol react with a sulfonyl chloride?

(Refer Slide Time: 01:34)



So, the general reaction of an alcohol with the sulfonyl chloride would be just to draw the molecule again; you have S double bond O, double bond O, Cl and I am just going to call this as R. So, an alcohol can react in the following manner. So, you have 2 lone pairs on the alcohol, so it can attack and go up, come back and kick out chloride and so the product that you will get would be R S double bond O, double bond O, O; let's call this as R^1 or R prime.

And, now keep in mind there is a positive charge on the oxygen because there is no source of base over here, okay. So, this is going to be likely one of the products that is formed and chloride and now you can think of a dissociation of H^+; it's a very strong acid. So, it's going to dissociate and give you the product which is R S double bond O double bond O O R prime, okay. So, this would be what I would expect as the product of this reaction. Now, these are usually nice solids you can isolate them, crystallize them, purify them and then use them for the next step which is usually a substitution reaction. But this types of sulfonates are themselves useful products in certain reactions, okay.

So, now, first part of the question we have sort of answered, in that the reaction of the alcohol with the sulfonyl chloride would give you a sulfonate. Now, there is another part to this question which is a stereo chemical part. So, what happens when you react this with a para-toluene sulfonyl chloride in terms of stereochemistry? In order to address this question what we shall do is we shall freeze the molecule in this conformation; so, once you freeze the molecule in this conformation then it becomes easy for us to answer the question, okay.

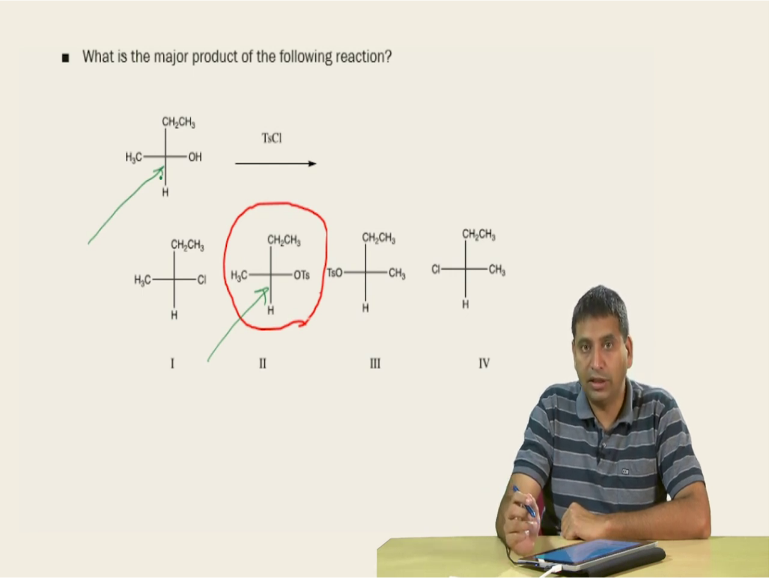
So, based on the mechanism as shown here we know that the absolute stereochemistry of this molecule of R prime (R') does not change because it is the oxygen that is reacting with the sulfonyl chloride. So, if the absolute stereochemistry does not change, then if this is R or S then the stereochemistry of the final product remains the same. So, this is retention in stereochemistry, okay. So, let’s keep this in mind when we are answering this question. So, there is retention in stereochemistry which is what we are going to see therefore, the configuration of this functional group over here has to be the same, okay.

So, if I have to look at this molecule there is ethyl on the top, methyl on the left, OH on the right and H below, okay. So, let’s now start ruling out the possibilities. So, the ruling out the possibilities, obviously, the 2 products which have chloride alkyl chloride can be ruled out because here you are not adding any nucleophile. So, if you add a nucleophile it is quite likely that it is going to react and give you the product, but since you are not adding a nucleophile there is not enough of the nucleophile in the reaction system to displace this.

So, it’s a choice between 2 and 3, okay. So, in order to address this we can go about by doing this in two ways. One is to assign the absolute stereochemistry that is you assign it as R or S and then look at the product, okay; that is one way to do it. I would recommend that all of you try this out I am not going to do that now, but you can go back and assign the stereochemistry, absolute stereochemistry for this molecule and then compare it with the product. There is one assumption that we need to make that is the relative preference for this OH should be the same as the product, okay.

Since your carbon is bound to either OH or OTs, the atom oxygen will get any way higher preference and therefore, we would assume that this and this will give you the same absolute assignment of configuration, okay. So, keeping that in mind now since OH is on the right, I would predict that II should be the correct answer, okay.

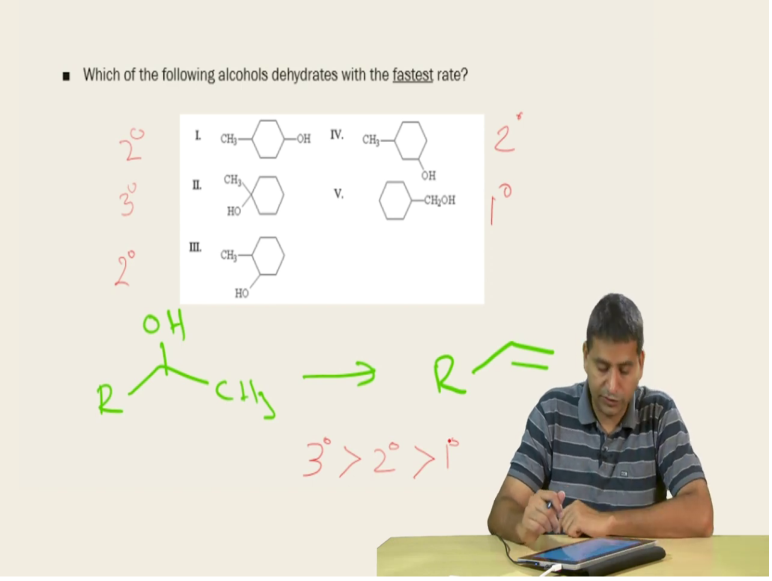
(Refer Slide Time: 06:30)



- What is the major product of the following reaction?

Now, let’s look at the solution to this and indeed it is II, okay. Now, I would recommend that all of you go back and assign the absolute stereochemistry for this carbon and absolute stereochemistry for this carbon and find out whether the answer is correct or not, okay.

(Refer Slide Time: 06:48)

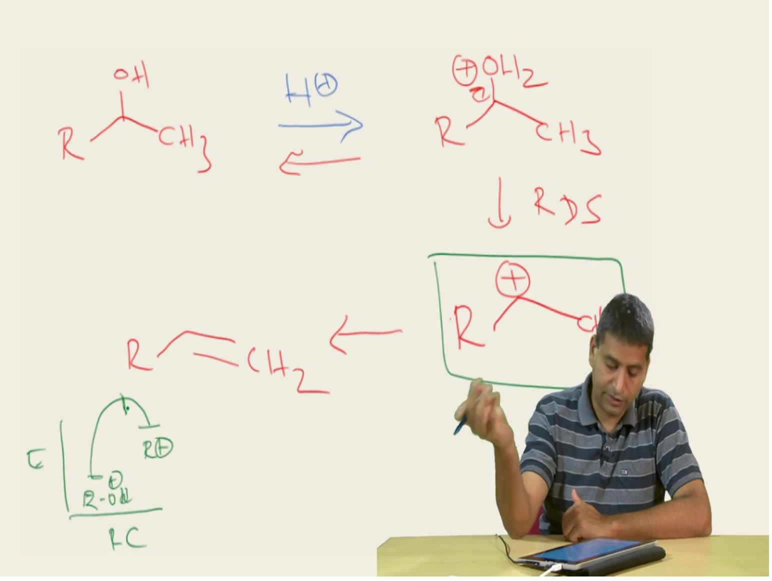


- Which of the following alcohols dehydrates with the fastest rate?

Now, let’s move onto the next question. The next question is which of the following alcohol dehydrates with the fastest rate? Okay. So, now, there are a bunch of alcohols that are given. Now, what is dehydration reaction? Dehydration reaction is a situation where you have loss of water, okay.

So, loss of water or dehydration is a reaction which will give you an olefin in this case, okay. So, the general reaction that we shall look at is R, let's say, CH_3 OH and this is going to give you R for example this, it can give you other products as well okay.

(Refer Slide Time: 07:32)



Now, if you want to look at the mechanism let's look at the mechanism in the following way. So, you have RCH_3OH and as you can see reaction dehydration would be conducted in acid. So, you would have a source of H^+ and this H^+ as being a strong acid is going to protonate the alcohol. So, you would end up with R OH_2^+ CH_3 and subsequently this would be lost as water to give you a carbocation, okay.

And this carbocation can now do multiple things and since we are looking at dehydration as the reaction you would assume that it's going to eliminate and give you this olefin or if R is also got some functional groups on it, I mean as some alkyl groups on it, it might eliminate to give you the more substituted double bond, okay. Now, looking at the kinetics of this reaction, it is quite likely that the first step is actually in equilibrium; that means, that you have an alcohol which in the presence of H^+ can get protonated and the protonated alcohol can dissociate and give you back the alcohol, okay.

So, this it is quite likely that it could be in equilibrium therefore, it's unlikely that it's a rate determining step. The second step wherein you lose water to give you a carbocation, this step is a high energy step because carbocations are in general less stable compared to the protonated alcohols. So, therefore, we would expect that this step would be the rate determining step.

Now, let’s go back and look at the starting various compounds that are shown here and what we will do is we will do a simple exercise of classifying them based on the kind of carbocation that is going to be formed. So, since this is a highly endothermic process that is it is a process wherein you are going to get an unstable carbocation, it’s possible or it is likely based on Hammond’s postulate that the transition state will resemble the product, okay. So, here in lies your carbocation and here in lies the OH_2^+ and this is energy this is the reaction coordinate. So, since this is a highly endothermic reaction the transition state will resemble the product, okay.

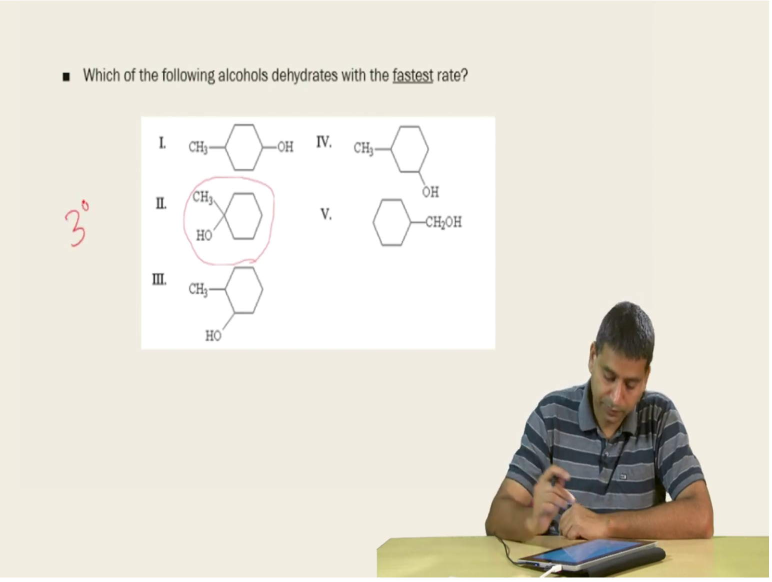
So, if we apply Hammond’s postulate in the situation then what will happen or what is likely to happen is that the stability of the carbocation or the product will play a role in stabilizing or destabilizing the transition state. So, if we follow along this logic, then a more stable carbocation should have a more stabilized transition state and therefore, more stabilized transition state will mean a lower energy which means that it is going to be faster, okay.

So, I will repeat the more stable carbocation is going to have a stabilizing influence on it and that stabilizing influence is likely to be felt in the transition state and so any stabilization influence in the transition state will lead to lowering of the energy barrier which means a faster rate.

So, therefore, our job here is to identify which carbocation of these is going to be the more stable one relatively. So, let’s do that exercise by classifying each of these as primary, secondary or tertiary. So, this choice number I is going to give you a secondary carbocation, choice number II is going to give you a tertiary carbocation, choice number III is going to give you a secondary carbocation again; this number IV is going to give you a secondary carbocation and number V is going to give you a primary carbocation.

So, we know from our previous experience that tertiary carbocations are more stable than secondary which are more stable than primary. So, if we follow this logic then it is likely that the compound or the alcohol that is going to produce a tertiary carbocation will react faster under these conditions.

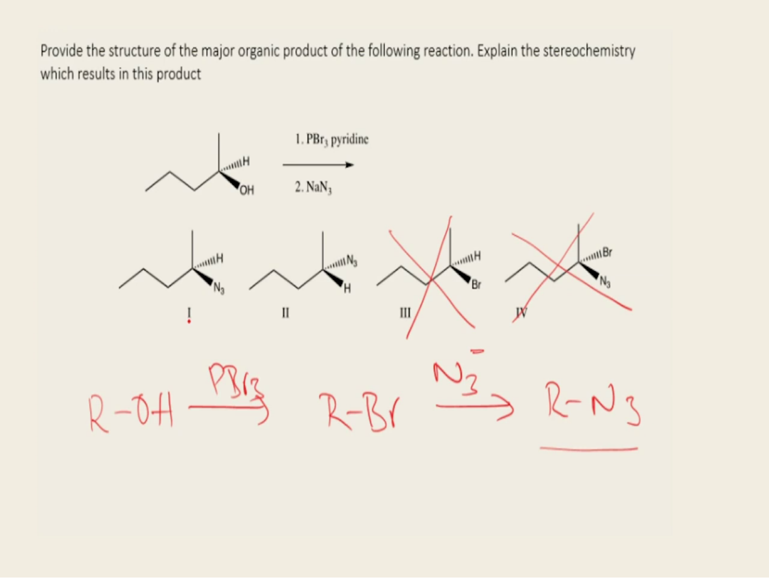
(Refer Slide Time: 12:14)



- Which of the following alcohols dehydrates with the fastest rate?

So, the correct answer to this would be choice II which forms a tertiary carbocation.

(Refer Slide Time: 12:23)



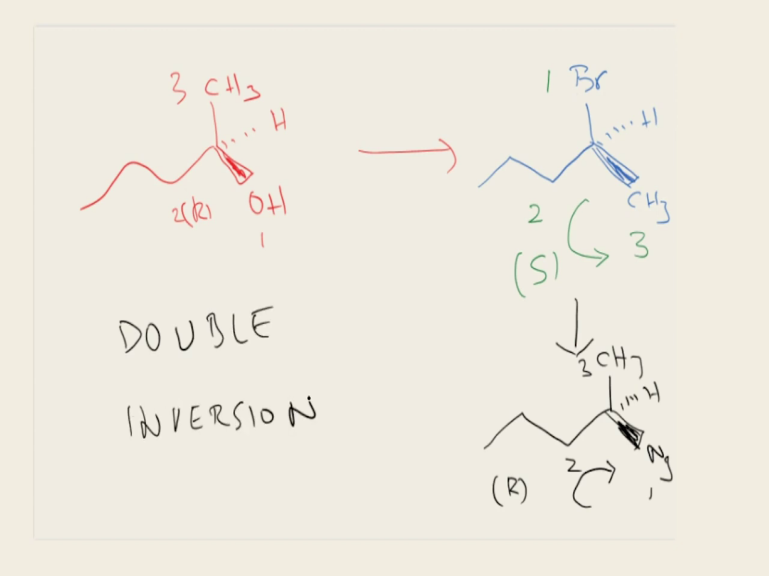
Provide the structure of the major organic product of the following reaction. Explain the stereochemistry which results in this product

Let's move onto the next question. So, here you have a reaction of an alcohol with PBr_3 and pyridine and the next step is reaction with sodium azide, okay. And the question is what is a product that is formed? Again there are 2 parts to this question. First is to identify the reactive groups and identify the possible reactions and part 2 of this would be to identify or to work on the stereochemistry.

So, now let's look at the first part which is the reaction of PBr_3, first we already know that PBr_3 reaction can occur on an alcohol and result in the formation of a bromide, okay. So, what is going to happen is let’s just look at the reaction giving you R-OH in the presence of PBr_3 is going to give you R-Br. We look at the stereochemistry very shortly. Now, when this reacts with sodium azide then you are going to get R-N_3.

So, the first thing that we need to do is to identify what the reaction is and what the possible products are. So, in these 2 steps, 1 and 2 we would end up with a azide as the product, okay. So, just based on this we can eliminate couple of these possibilities that is this reaction is unlikely that is you are not going to get a bromo azide, you are only going to get an azide and this is also unlikely that is giving you the bromide alone because you are reacting it with sodium azide. So, we have a choice between I and II okay.

(Refer Slide Time: 13:54)



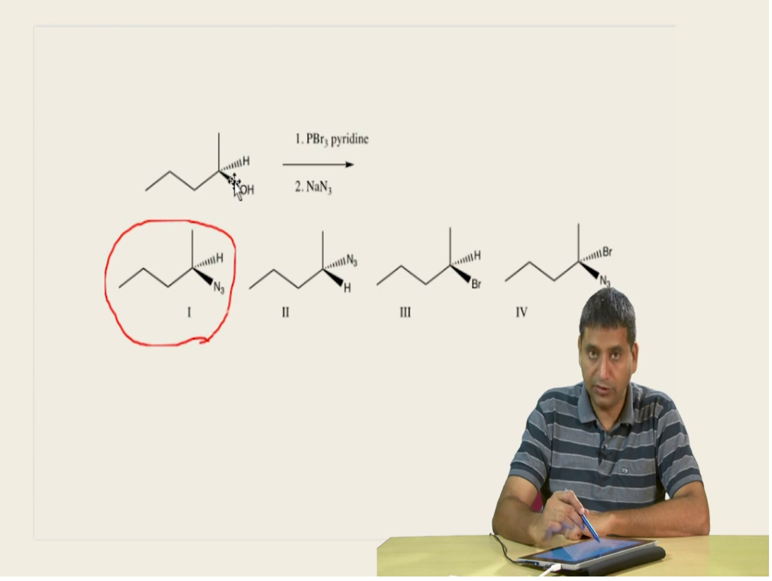
So, now if we were to see what is going to happen here is that let’s say we have in the starting material, we have this alcohol over here and I am going to redraw this alcohol and see kind of a bromide it’s going to give me, okay. So, if you redraw this alcohol, this CH_3 over here, okay. So, if I have to assign the absolute stereochemistry I would get, this is number 1, this is number 2, number 3, so this is going to give me R, okay.

Now, if it reacts with PBr_3 I know that it is going to result in an inversion of the stereochemistry. So, what I will simply do is to invert one of the molecules that is going to be produced and let’s say that it reacts from the back side I am going to keep this part constant and the Br, I am going to draw here; H, I am going to keep over here and CH_3 is over here, okay. Now, let me go back and assign the stereochemistry.

So, it is 1 2 3, let me write that down. This is priority number 1, priority number 2, priority number 3. So, this is going in this direction, so it would be S, okay. So, this results in the first inversion in stereochemistry. Now, we need to think about the second reaction with sodium azide and as you know sodium azide is going to do back side attack and it's going to result in the second inversion. So, you will get back a similar situation where N_3 CH_3 H.

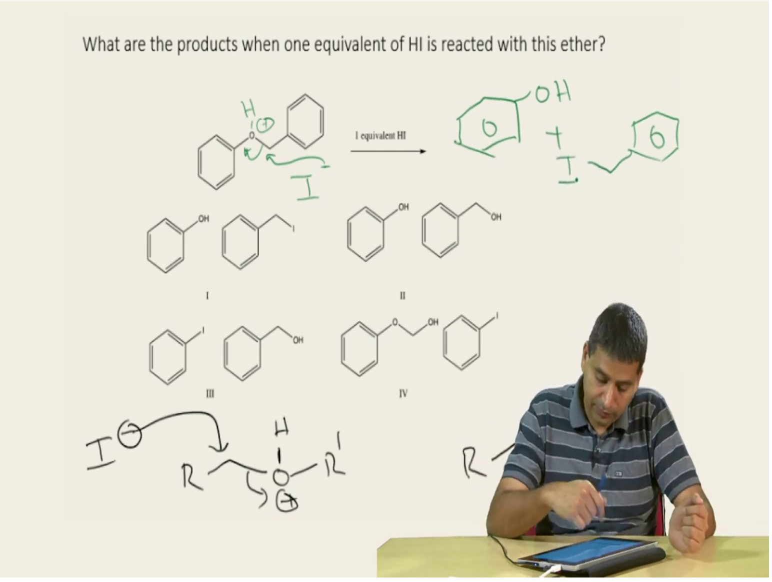
So, now, if I assign the absolute stereochemistry it is 1 2 3, hydrogen is going in. So, this is clockwise, so it is going to give me R, okay. So, therefore, this is an example of a double inversion reaction, alright.

(Refer Slide Time: 16:10)



So, therefore, I would end up with compound product 1 wherein the stereochemistry of this is identical to the stereochemistry of this.

(Refer Slide Time: 16:21)



What are the products when one equivalent of HI is reacted with this ether?

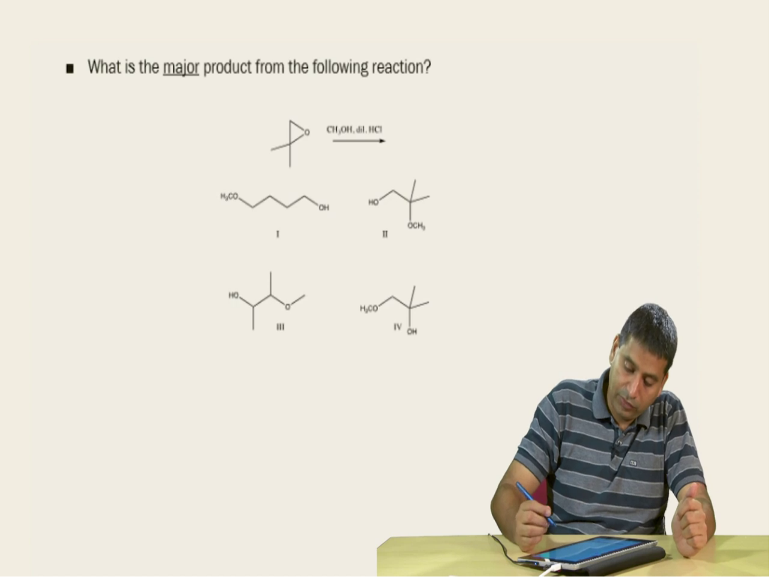
Now, let’s move on to the next question. So, here it is a reaction of this ether with HI and HI is an acid and it’s going to give you few products, okay. So, let’s look at the mechanism of this reaction; again if you have an ether, ether has 2 lone pairs, the oxygen has 2 lone pairs it’s going to react with H^+ and it’s going to give you a protonated alcohol.

So, by now we are now experts that we can predict that if you have let’s say R prime, it’s going to get protonated and give you OH^+, okay. So, now, in this molecule what you are doing is you are generating a pretty good leaving group, okay. So, therefore, it’s possible that since you have iodide in the mix, iodide can come and attack here and kick out this alcohol. So, R-I plus R'OH are the products, okay.

So, here you have a cleavage of an ether to give you an alcohol and an alkyl iodide, okay. So, in this particular case what is going to happen is you have this ether over here and this ether is going to get protonated. So, let me draw the protonated form OH and there is a positive charge over here and now there are in principle two choices for attack by iodide. So, iodide can attack from here that’s one possibility and it’s going to break that bond or else it can attack from here on this carbon, okay.

As you very well know attack on the aromatic ring or just on a phenol ring with no strong electron withdrawing groups is highly unlikely and therefore, the second possibility can be ruled out. So, therefore, the first possibility which is the attack on this CH_2 is more likely. So, now, let me erase this and draw out exactly what we think is the right way this can happen. So, you have OH, the plus charge, iodide attacks here and kicks this out, okay. So, you are going to end up with benzene ring on this side with an OH plus benzene ring on the right with iodide, okay. So, this is going to be the correct answer. Now, let’s look at the correct answer over here which is choice number I, okay.

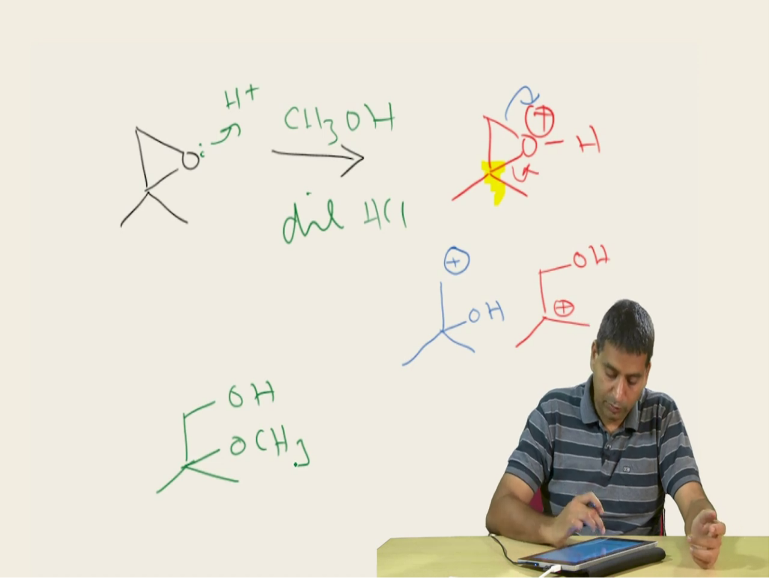
(Refer Slide Time: 19:16)



- What is the major product from the following reaction?

Now, let’s move onto the next question where you have the example of an epoxide opening. So, the question here is what is the major product of this reaction? Okay.

(Refer Slide Time: 19:29)



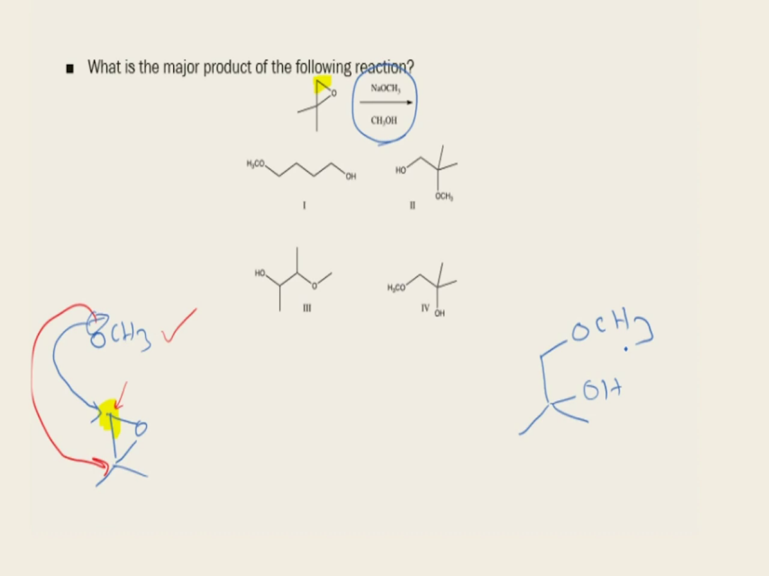
So, here you are opening up an epoxide as shown here I am just going to draw this out. So, you have an epoxide with 2 methyl groups and it’s exposed to methanol and dilute HCl okay;

so you have methanol CH_3OH and dilute HCl, okay. So, dilute HCl again one of the roles that you can think of is that it's going to produce a proton and so the proton is going to react with the epoxide and give you the OH^+ with two methyl groups over here. And now you are going to do this reaction perhaps in methanol and say you have a plenty of methanol that is going to be present and so methanol has to attack and open up the epoxide.

But before that it's quite likely that this bond if you break in the following manner you will end up with OH and a carbocation, right and if you open it from the other side you will end up with the tertiary alcohol with a carbocation over here, okay. Because we know that under acidic conditions there is a high likelihood that a carbocation can be formed. So, keep these in mind when we are looking at this answer. So, we have already discussed in class that epoxide opening under acidic conditions likely favors the attack on the carbon which can stabilize the incipient carbocation better.

So, therefore, it's more likely that the attack by the nucleophile will happen at this carbon. So, if we push that logic forward, then you are going to end up with OH OCH_3 of course, you would end up with the protonated methanol which is then going to lose a proton to give you this product. Therefore, I would predict that this is going to be the product that is formed.

(Refer Slide Time: 21:47)



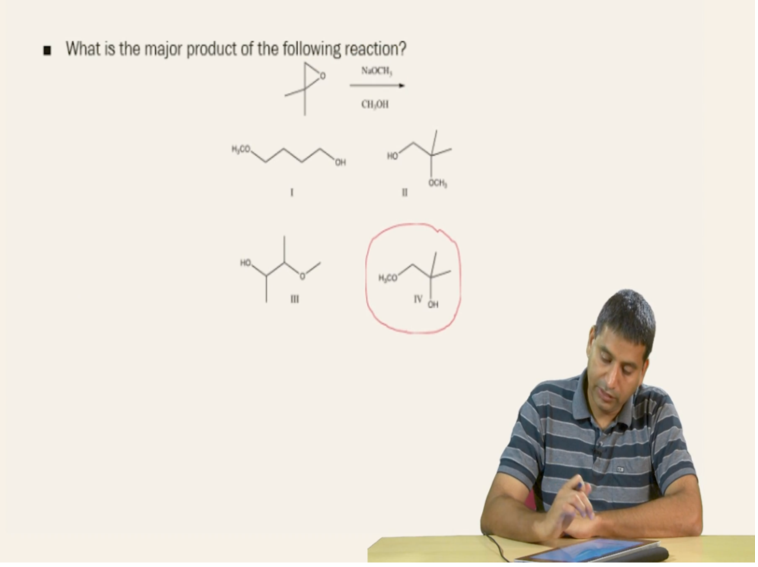
- What is the major product of the following reaction?

Now, let's look at the next question where you have a similar epoxide opening except that it is under basic conditions. You have sodium methoxide and methanol and so sodium methoxide and methanol is clearly a situation where you have a fairly reasonably strong base present in the system.

And, so here the logic is that the opening of the epoxide would have to happen under conditions which would favor an S_N2 like process, okay. So, you have OCH_3^- which is the nucleophile and so it has two choices, it attacks from this carbon or it can attack at this carbon, okay. So, if you look at choice number 1 versus choice number 2 the attack on the carbon which is a primary carbon is more likely than attack on the carbon which is a tertiary carbon, okay.

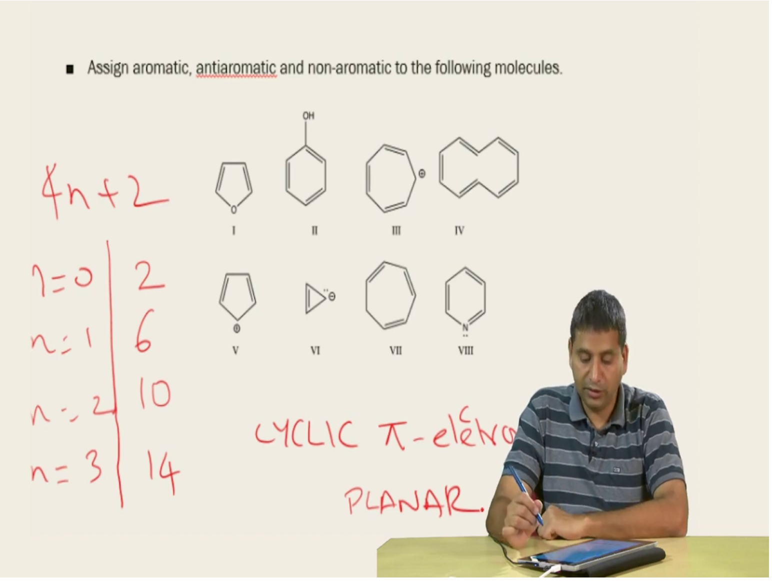
So, therefore, I would prefer the first situation where the attack happens on this carbon as shown here. So, therefore, this is the one that's going to react and the product that you are going to get would be OH OCH_3. Again don't get confused by this process, what do you need to remember is that under acidic conditions the epoxide is going to get protonated; the protonation of the epoxide is a very fast equilibrium process.

And so once you protonate the epoxide you are going to generate a carbocation and therefore, the carbon having the more stabilized carbocation is more likely. In the base mediated ring opening there is no carbocation formation. So, then the logic would be, that we would follow or the attack would happen on the carbon which is less hindered sterically, okay. So, keep in mind it just like S_N2 reaction and so the answer would be as shown here.



- What is the major product of the following reaction?

(Refer Slide Time: 23:47)



- Assign aromatic, antiaromatic and non-aromatic to the following molecules.

4n+2

n=0	2
n=1	6
n=2	10
n=3	14

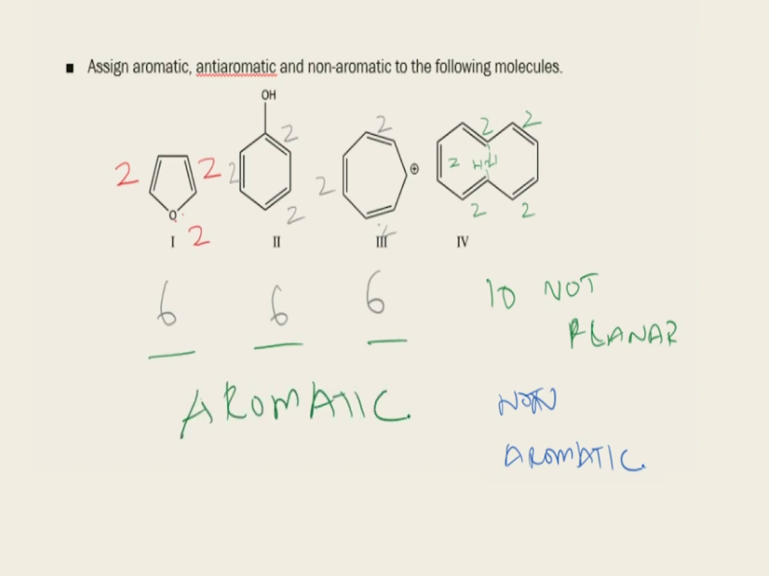
CYCLIC π-electro

PLANAR.

Now, the next question is we need to assign whether these molecules are aromatic, non-aromatic or anti-aromatic, okay. So, we have already looked at this in class, so we have the rule called the 4n + 2 rule. So, let me just write that down with n equals 0, 4 into 0; 0. So, the answer would be 2; n equals 1, 4 plus 2 would be 6; n equals 2, 4n would be 8; 8 plus 2 would be 10, okay.

So, n equals 3 we will just write it down, it’s n equals 3, 4 into 3 is 12; 12 plus 2 is 14 okay. So, what this rule tells us is that any cyclic system of pi electrons if it has this kind of numbers, then it would be aromatic and it has to be in a plane. So, therefore, the cyclic system of pi electrons has to be planar, right. So, using these criteria now let’s look at what happens with these questions.

(Refer Slide Time: 24:58)

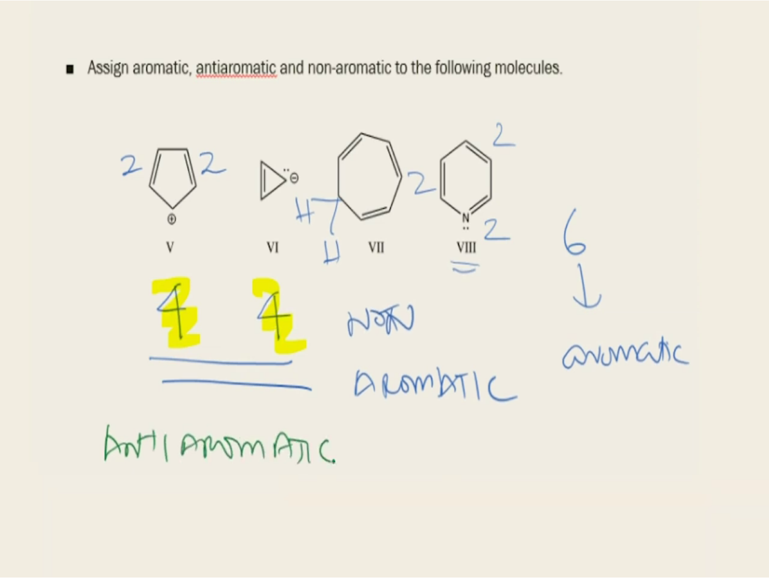


- Assign aromatic, antiaromatic and non-aromatic to the following molecules.

So, the first one here compound number I has 2, 2 and one of these lone pairs can be involved in cyclic system of pi electrons. So, you have 4n + 2 which is 6, okay. In the second case, basically this is 2, 2, 2 again 6; here you have 2, 4, 6 that is 2, 2, 2 and the carbocation is a vacant p-orbital okay. So, therefore, it is a cyclic system, it is planar and it is of pi electrons and therefore, this would be 6 electrons. Here in this case you have 2, 2, 2, 2, 2, but 2, 4, 6, 8, 10, so we have 10 electrons.

However, because these 2 hydrogens are very close to each other this molecule goes out of the plane so therefore, this is not planar. So, therefore, this would be non-aromatic, okay. So, these 3 molecules all 3 of them satisfy the criteria for aromaticity and therefore, they would all be aromatic. Okay, now let’s look at the next batch of compounds.

(Refer Slide Time: 26:22)

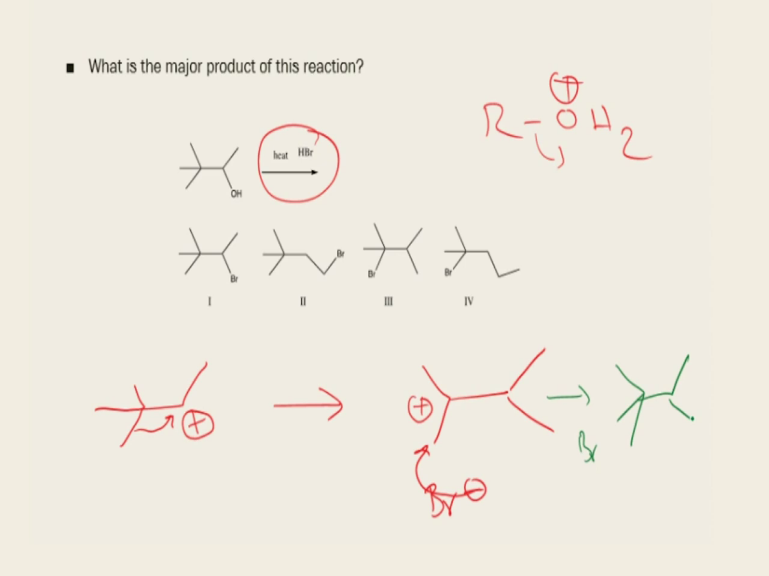


- Assign aromatic, antiaromatic and non-aromatic to the following molecules.

So, here you have 2 and 2 which is 4 electrons and here you have 2 plus 2 again which is 4 electrons and these both are planar. Now, coming here these are 2 hydrogens over here. So, there is no scope for a cyclic system of pi electron. So, therefore, this would be not or non-aromatic and lastly, here you have 2, 4 and 6. So, you have 2 2 2 and the lone pair of pyridine is actually orthogonal or perpendicular to the cyclic system of pi electrons and therefore, it does not participate and so this would be 6 electrons as well, okay. So, coming to the easy case of 6 of this molecule, this would be aromatic.

Now, coming to these two what we know is that when you have a 4 pi electrons then the molecule becomes anti-aromatic. So, therefore, these two would be anti-aromatic, okay. So, when you are looking at solving these kinds of problems make sure that you count the system of pi electrons correctly and second thing is to make sure that they are actually planar; if they are not planar then it is not possible for the molecule to be aromatic.

(Refer Slide Time: 27:49)



- What is the major product of this reaction?

Now, let’s look at the last question. So, here is an alcohol which is reacted with HBr which is under heating conditions again we know that when you have an acid and you have an alcohol, it’s quite likely that the alcohol will get protonated. So, you will have R-OH$_2^+$ which can then lose water to give you a carbocation, right.

So, therefore, what we are dealing with is a situation where you have the formation of this kind of carbocation and we already know that the shift of a methyl group is highly likely because it’s going to result in a tertiary carbocation, right. And now if this is the major carbocation that is formed, if Br is present, Br$^-$ can attack and give you the final product which would be this, okay. So, the correct answer would be this molecule which is molecule III, alright.

So, with that we come to the end of this tutorials; so, this as we discussed is the last tutorial. So, I hope you have enjoyed doing this course and if you have any questions please ask on the portal and we will be happy to answer. And we have another live session that is coming up right after this which will be announced shortly. I hope many of you will participate in it and please send your questions for that, okay.

Thank you, bye.