Organic Photochemistry and Pericyclic Reactions

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Lecture No. # 24

Sigmatropic Reactions – I

So, in the previous class we were discussing about the sigma tropic reactions, right. So, we broadly classify sigma tropic reactions as 1 n and as well as n number sigma tropic reactions. One n we said that the residue will move from the first position to the end position, and enum rearrangement we focus like it will be the movement of your sigma bond across your pi system. Then, in 1 n system we again broadly classify that as hydrogen movement system, and carbon migration system. So, we were dealing about hydrogen shift; so what we studied there, we studied like reactions like 1 3 1 5 and 1 7, and then we slowly got into their stereo chemistry.

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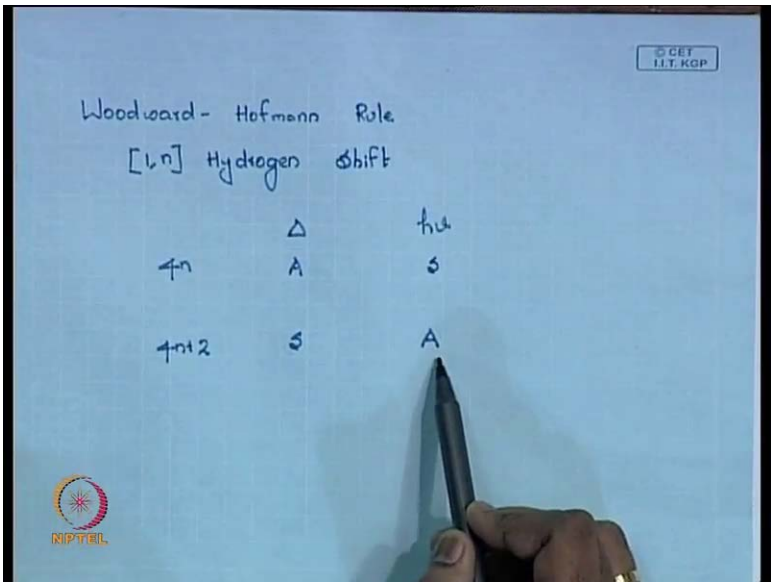

So, stereo chemistry may we studied two things, right. One, it should be suprafacial or it can be antarafacial. Then we had this Woodward Hofmann rule for your one n hydrogen shift. We said that we will take 4 n 4 n plus 2; I am talking about the number of electrons involved it will be pi system as well as sigma electrons, then I said heating and in the

light we said it will be antarafacial and will be suprafacial, and just it will be opposite to this.

So, what I mean is that if I take 1 5 system - 1 5 hydrogen system, it will be 6 electrons systems, so 6 electrons system if I heat it I might end up with a suprafacial, and on the light it will be antarafacial. And if it is a 1 7 system, it will be other way round, but the boss one thing you have to remember which has that 1 3 shift. In 1 3 normally you do not observe any type of reactions on heating, when it is light then you can see suprafacial, but on heating you do not see the any type of reactions we do not see 1 3 hydrogen shift, we will just see why it is?

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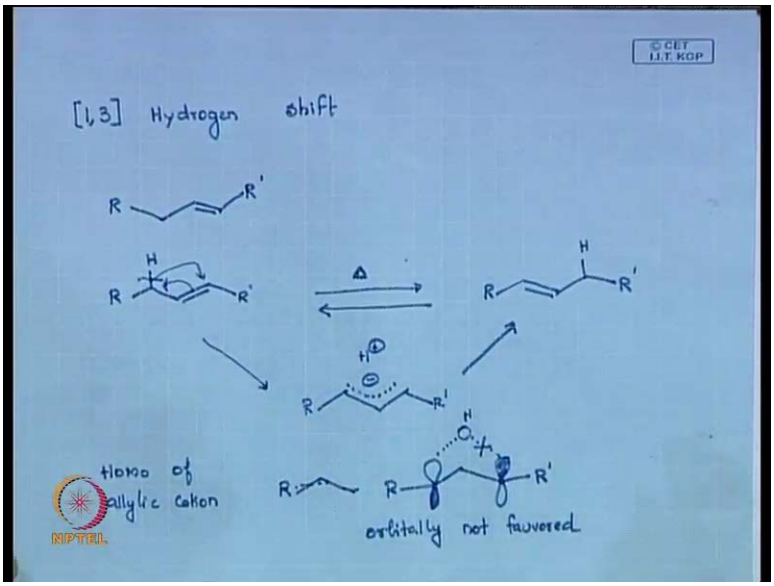

R prime better to write it, so that I have a system like this (( )) hydrogen, now if I heat this what happens? So by theoretically, I should expect a 1 3 hydrogen shift, right? So, if you feel this, how this reaction goes just for an assumption that it is the bond cleaves here, we think like it goes by a sort of radical it is not completely, because it is pericyclic; goes by transition state. If you for assumption, if you feel that reaction goes like this way, like get an cation and you can write as H plus, this can give you the product. If you feel of course, now I am dealing with this system; this is what? This is an allylic cation, so we are concerning about the heat. So, what we have to which orbital we will be looking into it, we will be looking into the HOMO of allylic cation right.

Just you draw the HOMO of allylic cation, how it looks like? One way of doing in a proper way is that you have an R R prime (( )), so this is my allylic cation which I have taken the HOMO of it 1 3, and this is my hydrogen. Now, if you see this reaction what happens? It has to go and if has to shift it has to shift like this, but if you see it is orbital not favored, so suprafacially it cannot do the process, because this orbital is not favored that is the rule again the rule if you put this in that Woodward Hoffman rule, it says yes, it should not be a suprafacial right that also matches with your orbital one.

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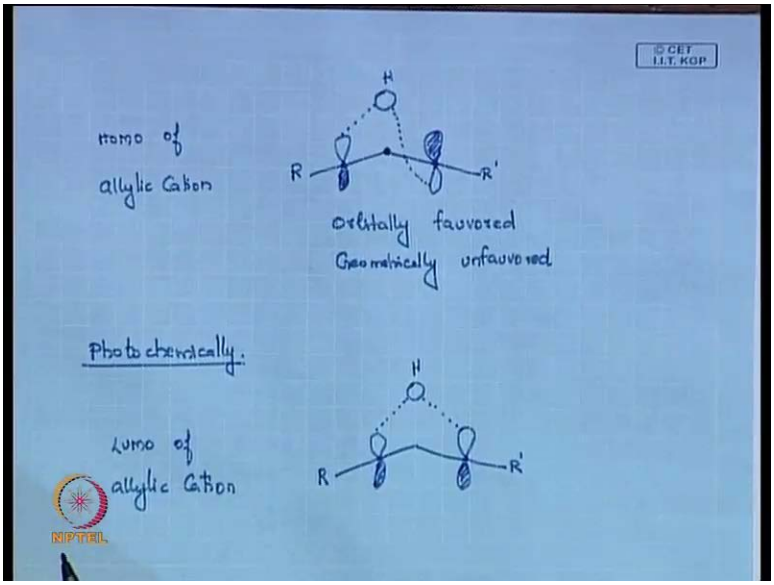

Now what I do is that same system, so this is your hydrogen so what the rule says it can be antarafacial, so it can do an invertion to come here, so your hydrogen can do this is because if you see orbitally it is favored, but what happens your hydrogen is very small it cannot bind it cannot do this binding, because it is very small that is why antarafacially also it does not occur even it is orbitally favored you can say geometrically it is unfavored because hydrogen is very small, so it cannot bridge between this two orbitals.

That's the only one exception that comes for this rule, otherwise it just everything fits to that rule 1 1 5 1 7; all this fit exactly only in 1 3 if you go for your heating both suprafacial and antarafacial does not occur, see if you see the same system photochemically. So, what happens in light, so in light I will be taking the LUMO of I will be considering the LUMO of allylic cation. So how to draw the LUMO, then so this will be the LUMO of allylic cation, you have your hydrogen fine, now in light it can

easily do this it can move suprafacially, because you see orbitally it is favored it can just move from this to this end suprafacially fine. So, same thae same thing you can do for your 1 5 1 7 everything, so this is orbitaly favored as well as geometrically favored. So, the reaction happens nice, so that is what 1 3 1 5 1 7 only one thing to remember 1 3 normally people ask this question all the time, yeah why 1 3 does not happen on heating the reason is that 1 3 by if you heat it geometrically it is not favored, because the hydrogen nucleus is very small to make a bridge between this. This point you have to remember fine.

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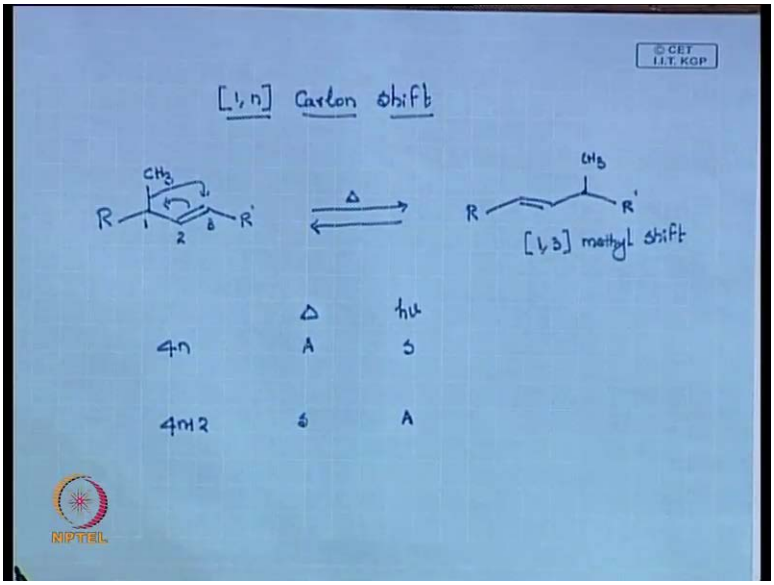

So that is about your 1 n hydrogen shift, now we will move to your 1 n carbon shift if methyl moves, then usually it is methyl shift we will start with the simple example read this. So, we will get a so this will be 1 2 and 3 (( )), so you can call this as 1 3 right because it moved from one to third position, so you can call it as 1 3, and here you can call them as methyl shift 1 3 methyl shift. So, fine so same way you can draw for your 1 5 and 1 7, and as you did for your hydrogen shift, now then comes your stereo chemistry into question whether this will be suprafacial or it will be antarafacial. See, if you just take a methyl system, then you can write the same rule like for your Woodward Hoffman I can write just like your hydrogen shift this also obeys your similar like your hydrogen shift initially it will be antarafacial 4 n, then it will be supra 4 n plus 2 reverse of it see just similar to your hydrogen shift when it is methyl keep that in mind when it is methyl. any doubt up to this.

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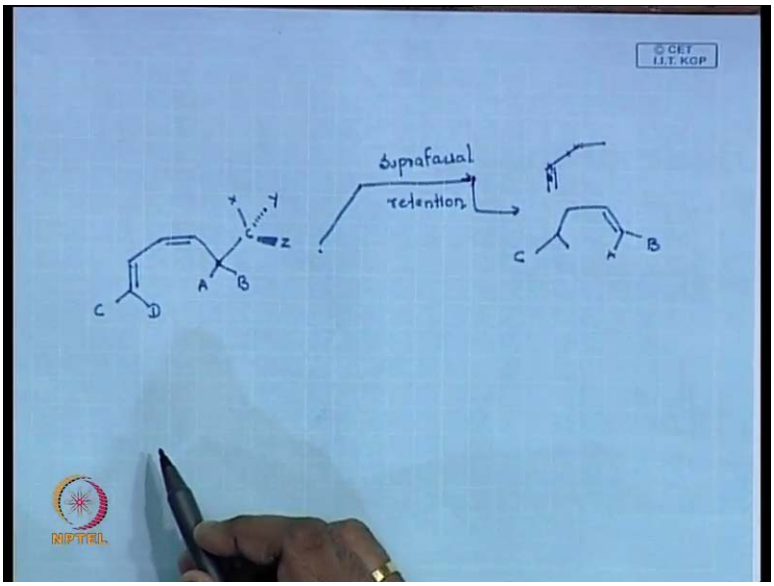

See the one interesting aspect comes in this carbon shift is that for example, I have a system I have system like this now what happens your carbon is sort of chiral, I am taking as carbon previously I said it is only a methyl shift where your carbon has 3 hydrogen's. Now, I am slowly introducing another concept where your carbon becomes sort of a chiral, now what happens if you the if you look at the stereo chemistry. What it can happen? First you will say that how it will be suprafacial, yeah what are the options you can write down one I can say I can write suprafacial keeping in mind, now my chiral carbon can be in retention one you should be in retention one option is there I can superficial retention can you draw that, because it is a 1 5 hydrogen shift can you draw this what ibis have written 1 5 hydrogen just sorry a then you get A B. Then you get A B then you have your C just try to draw this suprafacial retention.

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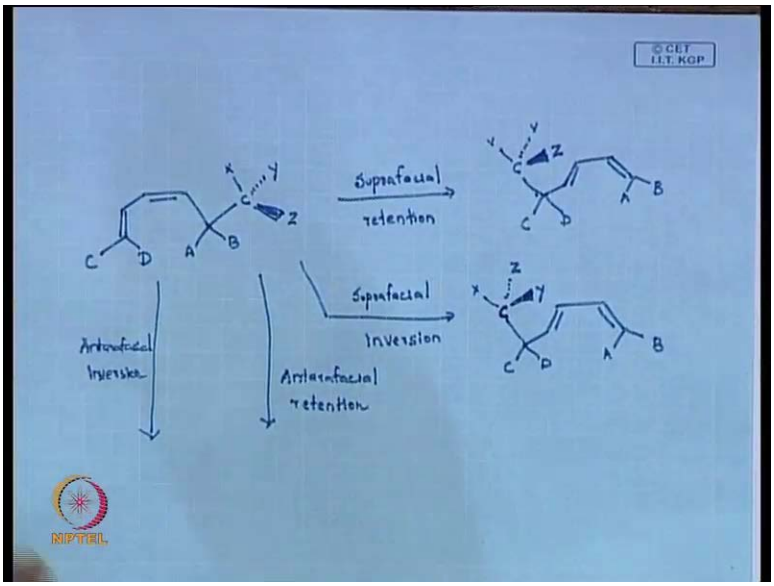

Just I want to see just I will come back I will take a new paper you guys try it what are the things you can draw C have A D suprafacial retention A B, because it has been shifted from your then you write your C here D. Now, make sure that your carbon that you are writing this is what now your carbon is having the same configuration that is retention, so another option can I write suprafacial invertion you can think about suprafacial inversion can also happen. Now, we are just saying that what are the possible options can be…

I can have an invertion (( )) then what we can think about, so I have a suprafacial retention suprafacial invertion, and then I can write anyhow I can write antarafacial yeah very good you can write antarafacial retention, so antarafacial retention will be just in the downright with a carbon. So, C and D will be up and your methyl will be in the down, and then you can write your antarafacial invertion see once it comes to a carbon which is type of which is a chiral, then you have to think about this 4 possibilities. So, one it can be suprafacial retention, suprafacial invertion, antarafacial retention, and antarafacial invertion see most of the time, if you do you get suprafacial retention when it is suprafacial most of the time it will be retention, if it is antarafacial then it will be invertion, this suprafacial retention and antarafacial retention more or less are same.

So, you have cases where you can get suprafacial invertion, this cases these are comes only in one case, if you take the rule most of the time you will end up with suprafacial, if it is suprafacial it will be retention, if it is antarafacial it will be invertion clear.

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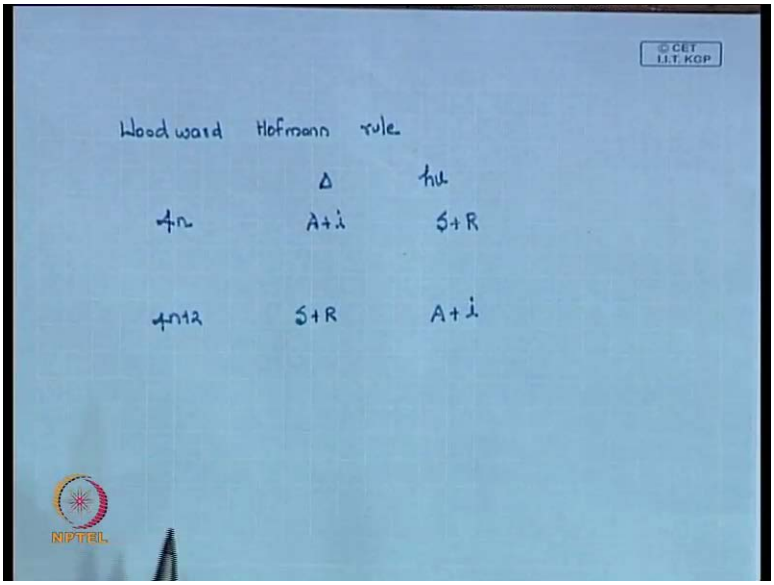

Now, what we will do we just take that Woodward Hoffman rule, which we wrote earlier for methyl shift that is 4 n plus 2 (( )) what we said we said initially it will be antarafacial, then it will be suprafacial - then suprafacial antarafacial so what we found out if it is a carbon with a chiral, if it is antarafacial it should be invertion. So, I can put A plus i if it is suprafacial retention, because it suprafacial there will be no change in your chirality, so it will be S plus R.

Fine now I just add one term into your carbon shift, if it is a just a methyl shift no need to worry it will be similar to your hydrogen shift, but if your carbon is a chiral. Then you have to understand whether is an invertion or it is a retention fine, so the rule can be done like this for 4 n it will be A plus i or S plus R 4 n plus 2 S plus R or A plus i clear, any doubt. Here see as we said in hydrogen shift for 1 3 hydrogen shift, when you heat it there is an exception that it does not undergo any reaction same way for carbon 4 1 3 heating, it does not follow this rule whatever rule we have written.

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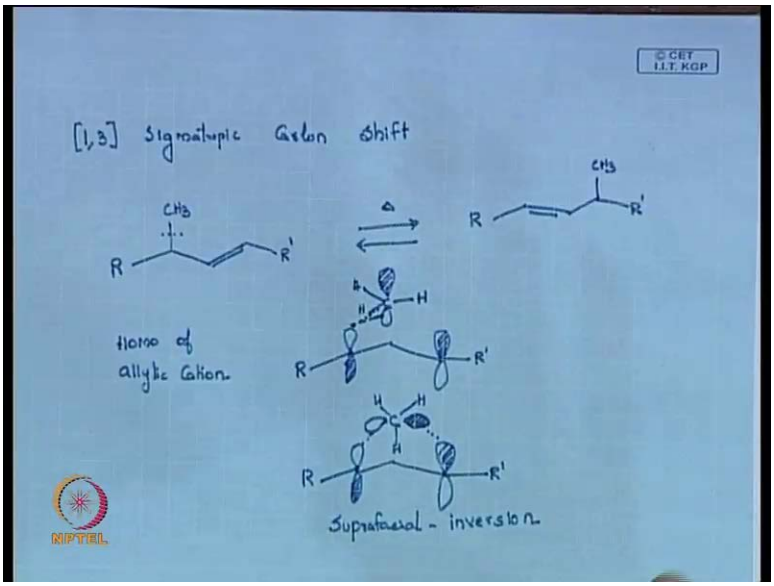

So, we will just see what it happens in that case; for example I take our 1 3 just sigmatropic carbon shift just taking on 1 3 for (( )), we will just take methyl for simple representation you will understand later why, so it is a 1 3 shift you know it goes by allylic cation. As a earlier said if I break this shall we draw the HOMO of this, because I am doing in heating, so I am just considering the HOMO of allylic cation, so how the HOMO looks it should be just the opposite right (( )). Now, I have to put my carbon sorry I will do put this, now you have your I just dram a carbon here fine, now you know that this is not going to happen, so what the rule says so it will be antarafacial invertion right. See the according to rule it should be it should make a antarafacial invertion, yeah looks like to be, because it says it can be but this methyl is… So, nice instead of doing this big thing what it does it simply invert itself, here if you just see this how easy it is for this guy to do this feels.

So, nice to see how these guys work so what it did is just inverted itself, now it can do easily suprafacial right why it does not do now antarafacial, because the orbital is favored see actually by rule it should go antarafacial invertion right, but what happen in this case you get suprafacial invertion. So, this is the only one case I think you get suprafacial invertion most of the case, if you say you will be dealing with suprafacial retention and antarafacial invertion yeah, because antarafacial you get invertion suprafacial it maintains. So, this is the only case where you get suprafacial invertion, so keep that in mind yeah yeah, see I am just taking for or an example simple, if it is X Y Z

it will be clear, but we are not seeing the difference because but actually it happens suprafacially invertion, you are not it happens like that you are not observing by the product, because yeah if you have a chiral carbon defiantly you can observe it will do suprafacial invertion. And you can clearly observe that from the product yeah, it is only for 1 3 sigmatropic shift, that also particularly in heating.

So this heating 1 3 heating in both the cases hydrogen as well as carbon does not fit exactly with your rule that only point you have to remember, clear, any doubt with this no so shall we get into problems.

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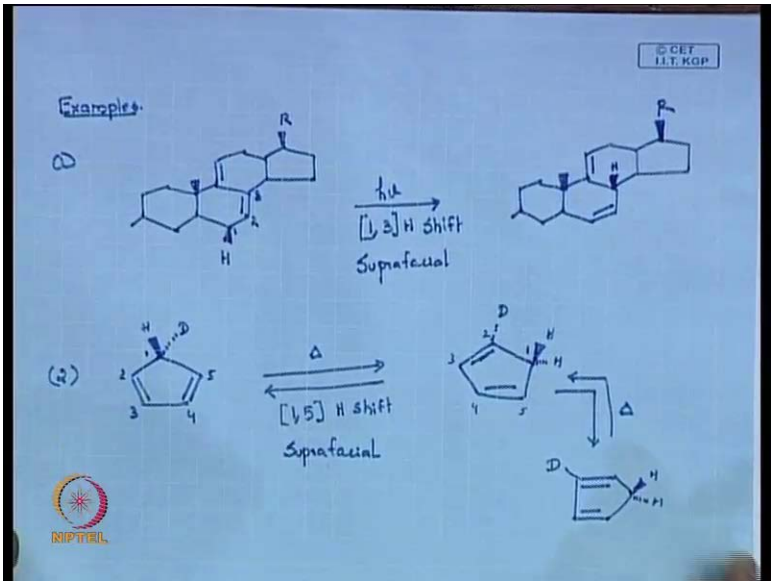

So, we will do some problems on 1 n sigmatropic shift I can say examples or I say problems see when you are going to write stereo chemistry is very important, because we are going to talk about. So, I have a system like this just I am going to fortalize, now first thing you have to find out whether what shit it is the second thing you have to find out the stereo chemistry alright, because I have to find my hydrogen. So, shift you are going to because this is fortalises I have defined the condition, so H mu which is possible 1 3 H mu 1 3 is very fast see 1 5 heating by other 1 7 again H mu, because these are all orbitally favored one. So, you can do the 1 3 hydrogen shift, the second question is that whether it will be antarafacial or suprafacial.

So, what the rule says what system it is 4 n, so light it is S suprafacial, so first you write that then you write the product once you finish it, so it is 1 2 3 right, so how your

hydrogen will be in same phase simple example, but tells you what happens clear, you have S system like this. Now, I am saying that I am going to heat it, what you are expect think of heating this system, see you have an option if you count have 1 3, and you have 1 5 that is a all should be 1 3 or 1 5, and I am giving heating you are just seeing which orbitally favored or 1 5 is favored, so it undergoes a nice 1 5 hydrogen shift, so 1 5 heating what it is antara or suprafacial just keep that formulae into your mind.

So, then I can write the numbers 1 2 3 4 5 right, so it is a suprafacial right you can get this any doubt? Again you can if you heat this, what happens? I can again heat this you will end up same 1 5 hydrogen shift, but not the same product, but same chemistry 1 5 hydrogen shift supraficially write the product number it you can write the product, see 1 2 3 4 5 my hydrogen can come here very good examples to work on which (( )) due to no hydrogen moves very, very fast compared to a its good. Then you can also move, so a we do not need to go by one by examples, we just change otherwise it looks like easy to find out.

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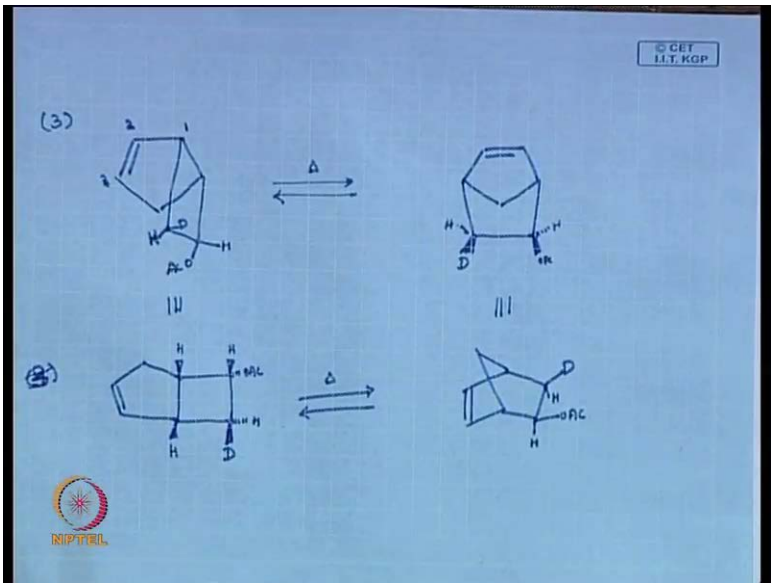

So, now I heat this what you look for see the hydrogen (( )) are on one side (( )), so this is O A C versitiale hydrogen, this is your hydrogen neutrium O A C and hydrogen, so what you observe now I heat this guy or if I fertalize, whatever if it is just heat it what you can think about there is no hydrogen you are thinking about hydrogen shift yeah, you can think about your carbon shift 1 2 3 this carbon (( )), so it will be 1 3 carbon shift,

so what it is what the rule says it will be an invertion. So can you write it, so it should be invertion keep that in mind, so if I will be happy if you write the structure before me, because it will I want to know how you see this particular carbon when it moves coz its undergoing invertion.

So, I know that you will write this part, but I will be much interested to see how you write this so you have a O A C, and you have an hydrogen here that is fine, because it stays same like that what happens this side. Now, what will happen to this hydrogen, and neutrium it will be other way round, because your inverting right. Now, you can write your neutrium here, and you can write your hydrogen see that is how you should know because this invertion, and retention has very big in writing the stereo chemistry it is not only about hydrogen shift or methyl shift or 1 3 or 1 7 it should be with your stereo chemistry fine, any doubt?

Take one another good example here, so whether you guys can write this the same one, but O A C just I am taking the same example just want to see again how you write this the way different way I am, yes, it is a same one right see that is what I am saying the way of projection it is the same example the way of projection is like this. So, do not think like when it is projected it is the different example, it is the same example that is what I want to know, so when you write you can open up this. And then also you can draw your stereo chemistry same way for this product, if you write in another way see I am just it is can say this 3 same way I am writing it now whichever way you like can open it up, and I am seeing people writing like this also that is also good way of representation right. Same example different way of writing it out the same compound, so you should know the many ways of seeing the molecule, that is why O just want to write this one right.

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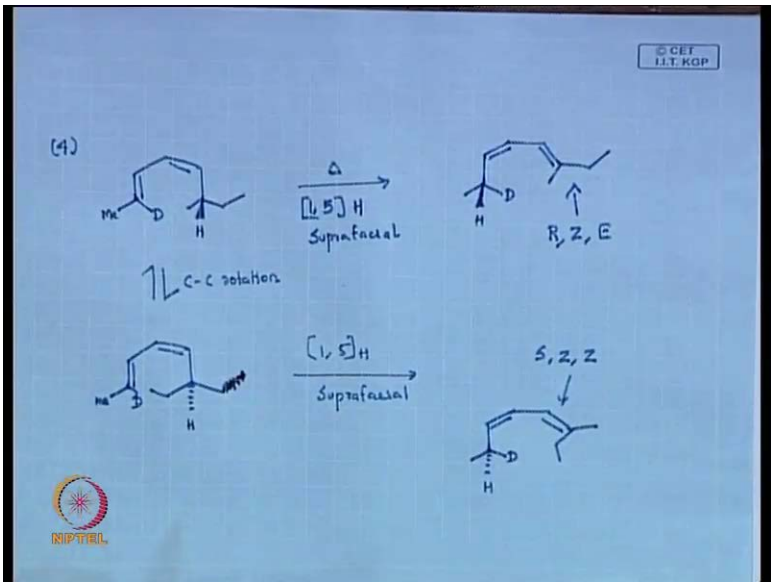

Now, we will take a good example for test of Woodward Hoffman, see you take this example if you heat this for example, what you should get I take this example and heat it, so it is 1 5, because where (( )) is 1 5 - 1 5 heating is what suprafacial right yeah. So, can you draw the structure, so it is simple, so it is suprafacial, so I need to add hydrogen, so it should be what if I number it R, this is R, Z, and E. See what happens is this compound once you do the heating I get another product which is S Z and Z also along with this. So, I get R, Z, E, I am getting S Z Z, so that means I am getting different stereo chemistry stereo (( )).

So, how it is possible any idea 6 membered, now if I just heat I get R Z that is you say as 1 5 hydrogen shift with a suprafacial or you are thinking for getting this you are thinking like antarafacial, but antarafacial never happens in 1 5, so what happens there? What happened to this molecule.

If you take in solution this molecule, so this molecule does very nice C-C bond rotation single bond rotation, so you sorry this is (( )) , you can have other way round, so just it can do a C-C bond rotation that is possible right. And this in 1 5 undergoes, 1 5 hydrogen shifts suprafacially, it will give you the other product which will give you the other product S, Z, E; that is what? See the nice way of writing it, so these are things you should know I am taking a molecule it undergoes C-C bond rotation, so it can give this these are all the options which are open when you do this type of examples. So, suddenly

don break the rule and say no sir it might also go in invertion I will get this product it does not happen that.

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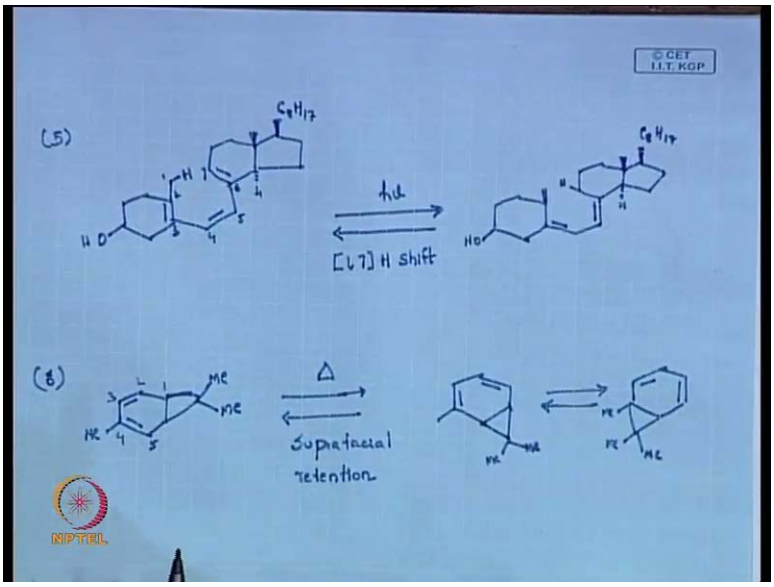

We will take another molecule. This molecule you have to say, because where you have studied you have studied this molecule in lot of places, any idea where you have sorry, you have methyl there, 1 2 you have methyl there, you have studied this synthesis where you have studied it has then it does a electro cyclic ring enclosure or you end up in sort of a vitamin, you have studied this in vitamin D synthesis right. What shift you study there see this if I do a fortalises, see when people ask they ask like this only fortalises what do you expect this? Sis trans sigma tropic any sigmatropic reactions any sigamtropic that we are dealing with sigamtropic only we are dealing right now with hydrogen shift on metals shift anything comes in your mind. See if I write this hydrogen, then things will come to your mind, if I write hydrogen like this that is what happens 1 7, see if I do not add write that hydrogen then you have to think.

See, if you have methyl just please write the hydrogen then it is easy to find out, it will be nice 1 7 you can write one 2 3 4 5 6 7, they are nice 1 7 hydrogen shift antarafacial or suprafacial that is very important. So, 1 7 hydrogen shift, so what your role says suprafacial 1 7 - 1 7 is what 1 7 is what system what electron system 4 n system (( )) yeah, because this geometry is little bit unfavored for suprafacial this should be just check it up I will get back to this regarding the configuration, because this geometry is

littile bit favored looks like to be in antarafacial looks to be antarafacial geometry I will get back to you in next explanation (( )).

You have S system like this now, now I say that I need a other way round I say that this chemistry goes suprafacially retention, what it says I am saying it is suporafacially, no you have double bond example 5 sorry yeah yeah sure. We need a double bond you shift this you shift that here right, so I want this reaction this reaction goes by suprafacial retention, so tell me what what condition it is other way round this is suprafacial retention this geometry.

So, what condition shall I use, because first you find out what shift it will be what shift you want to do 1 2 3 4 5 right, so I can move this carbon so it will be 1 5 shift so 1 5, if I want suprafacial retention what I have to do heat it or fortalize. See, that is the other way of finding out see one way I can ask you the that heat what you get otherwise I can ask you that this is the geometry I got, so find out the condition you should do other way round also, now heating you just draw the structure. So, it should be a methyl here, so further also you can do this same way, then what you get again same right any doubt with this systems now.

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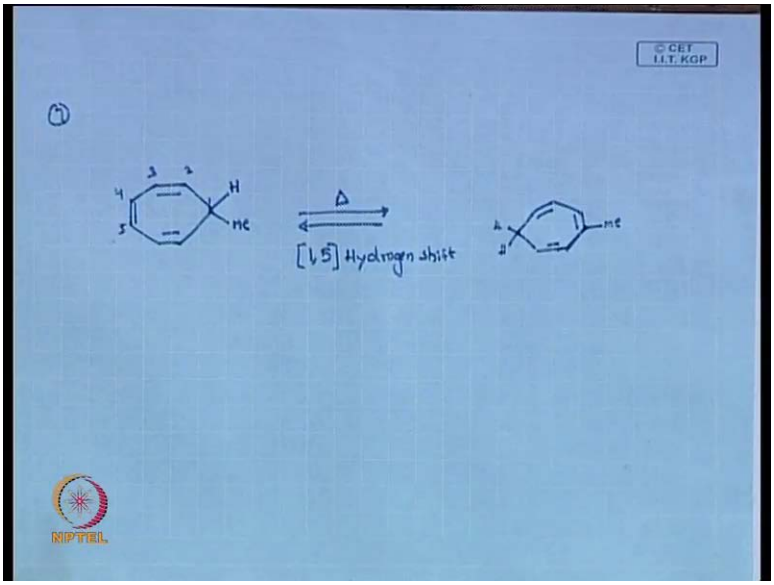

So, you can do any examples then now I will give you one example which you guys should try to do. I have a system like this; I have many combinations here. I say that I am just triplating it for heating; what you want to do? Heating, so 1 5 what 1 5 there are 2

choices - methyl or hydrogen. I can push my methyl; I can push my hydrogen; what you want to do?

(( ))

Yeah, 1 5 hydrogen shift? Very good; so 1 2 3 4 5; see now, you know how it is, right? You have your hydrogen here; so now you have you have conditions.

So, you see if an example is given, you have to find the condition. If the condition is known then you find out whether it is 1 5 1 3 1 7; then you find out whether it is suprafacial or antarafacial. Then you find out whether it is a retention or invertion. Any doubt with these examples? So, we will stop your 1 n hydrogen shift; that is all on 1 n hydrogen shift; we will be then concentrating on (( )) sigmatropic reactions.