Organic Photochemistry and Pericyclic Reactions

Prof. N .D. Pradeep Singh

Department of Chemistry

Indian Instute of Technology, Kharagpur

Lecture-23

Introduction to Pericyclic Reaction

Yes; so for we have discussed about some important aspects of photo chemistry. In the coming classes we will be discussing more about pericyclic reactions; we will concentrating some we will concentrate on some important reactions.

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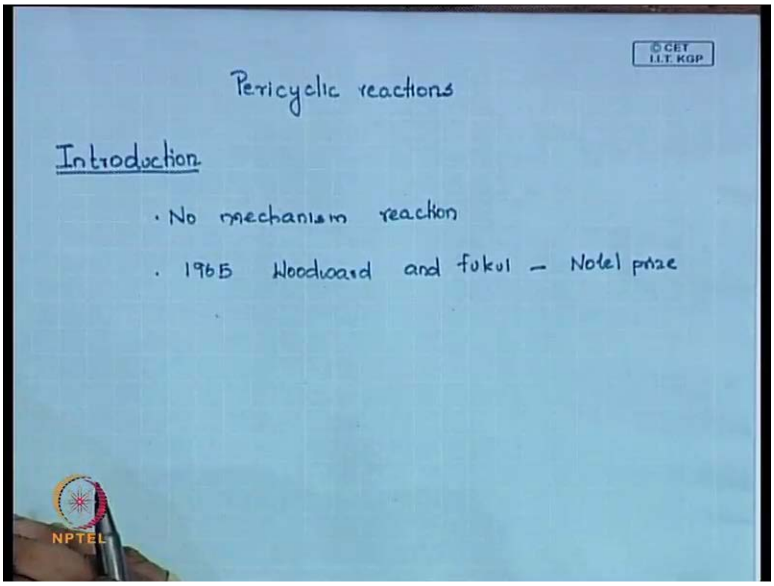

Pericyclic reactions

Introduction

- No mechanism reaction
- 1965 Woodward and fukui – Nobel prize

So, this half we will be concentrating more on pericyclic reactions. Just I will get you some nice introduction of pericyclic reactions. See this pericyclic like early times people thought that these reactions go by radical or it goes by ionic items like cat ion or an ion they were they were not up thinking about a reactions where there is no intermediates.

So, they come across certain reactions which were not affected by solvent, which were not affected by pH and after lot of struggle they were not able to isolate any type of intermediates. So, these type of reactions they call them as non mechanism reactions; they just call them as non mechanism reactions. But, you have after Woodward he was working on these steroid chemistries, he found out or he observed an important aspect. When you take steroids and if you heat it we get nice selective steroids but, once you take the same chemistry and do it in light he observed different isomer in selectivity in that. That was very important observation seen by Woodward; so what he did that Woodward as well as Hofmann, you heard about Hofmann and Hofmann is a great theoretician and he was working on quantum. Woodward and Hofmann then came together, formulated a rule called as Woodward Hofmann rule which decides the steroid chemistry of these reactions and they coined them as most like pericyclic reactions.

At the same time, you heard about Fukui; he was also contributing lot on this understanding about this pericyclic reactions. I think in the year 1965, Woodward and Fukui they shared Nobel prize in chemistry for these pericyclic reactions.

The pericyclic reactions have a very good important lethality in synthetic chemistry like your C-C bond. You can do that what is the famous reactions in pericyclic where you do C-C bond formation cycloaddition and your deals had reactions. You can do many synthetic application using deals had a reactions there were ene reactions you have Clyde’s and Lee Reherman scope here. So, they started having more important in organic chemistry; so, that is the sort of introduction to pericyclic reactions. Now, we will see that how we can define these pericyclic reactions.

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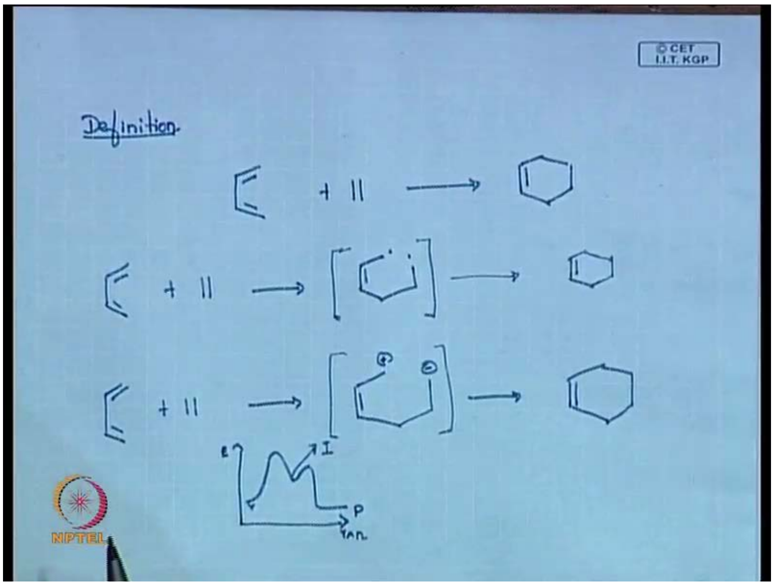

How we can define these pericyclic reactions? Normally, I am taking simple reactions which you have known. Take this, you can get this product right; see, if you are not having an idea of pericyclic, let me assume that this reaction goes by sort of… if I can write that reaction goes by radical if as, if I assume is that true, if I assume then I can think about making the same product, right? I can call this as intermediate or same reaction I can assume in other way also.

So you can see, I can see the, I can feel this reaction like this but, the interesting part of this reaction is what this reaction is more like an intermediate reaction; it is a step wise mechanism. If you want to write energy profile for this reaction, how you can draw a energy profile? Basically, I have my reaction coordinate here I have my energy.

If I want to draw my energy profile like my reactant and my product and this is will be my intermediate, so you say this reaction like step wise mechanism which goes by a type of intermediate on other hand if I take the same reaction.

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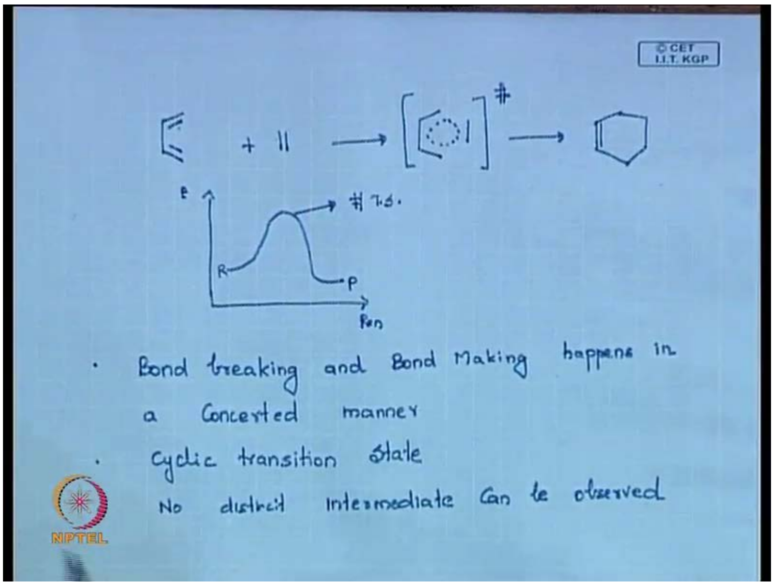

- Bond breaking and Bond Making happens in a Concerted manner
- Cyclic transition State

No district intermediate Can be observed

Say that I so it call this is a transition state because, it is not a intermediate which I can isolate. So, how you can think about the energy profile so it will be, I draw my reaction, it will coordinate with my energy? I have R, have my P and this will be my so called transitions state right.

See you have a free, you can think about a step wise mechanism where you have an energy profile with an intermediate impact and you think about your reactions which goes by like without radical intermediate goes to a transition state; you end up energy profile like this; so with this can we define now pericyclic reaction with this idea.

The first thing comes in your mind is what your bond breaking as well as your bond making process, right. Your bond breaking and bond making happens in a concerted fashion or concerted manner, right. So, you can see the bond will be made here; same time your bond can be broken. So, both happens very concerted and it is simultaneous so that is the first thing about the pericyclic reactions. The second part is that your pericyclic reaction goes to a cyclic transition state.

The third is that you will not observe, no distinct intermediate can be observed. These are the 3 important things which you know about pericyclic reactions. So, that is how you can define pericyclic reactions first point you say that bond breaking and bond making happens in a concerted fashion the second point you say that it goes that cyclic transition state. Finally, you say you cannot observe any distinct intermediate in this reactions that is very formal definition of pericyclic reactions.

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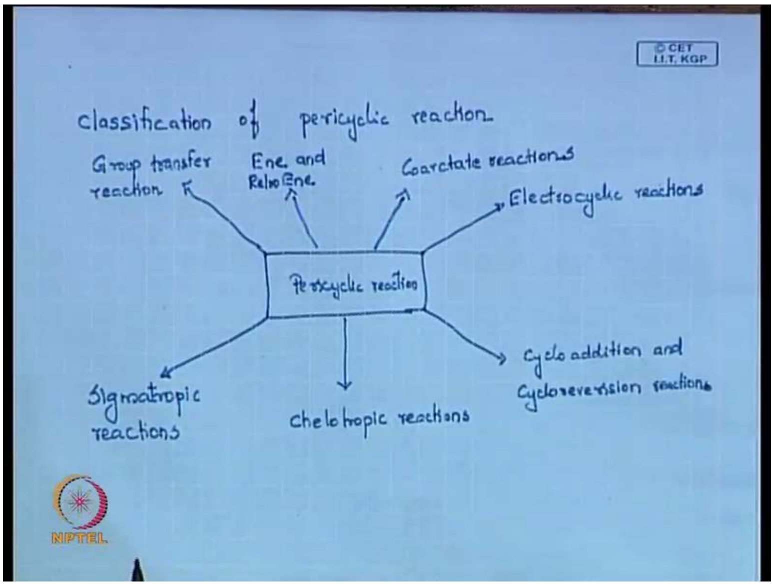

Now, will see classification of pericyclic reactions based on Woodward pericyclic reactions can be broadly classified in 5 major reactions. There are 5 major and 2 are minor which you can incorporate into a pericyclic but, if you say broadly they are 5 major classes.

One is your electro cyclic reactions, very important class where you study about your con rotatory and disrotatory ring opening and ring closer that is very important there and then you study about your cyclo addition and same way you study about your cyclo reversion reaction important class of your pericyclic. Another you can think about is your sigma tropic reactions and you have your group transfer reactions then, have your steroid tropic reactions. These are your 5 major classes which you see in pericyclic electro cyclic where you study your con and this right ring opening and ring closer cyclo addition reactions. You study your famous 2 plus 2 then, you study your 4 plus 2 ( ) reactions; retro deals had a… where you study about cyclo reversion reactions, right.

Sigma tropic you study your 1 coma that is your hydrogen shifts and carbon shifts metal shifts; then, you study your cop claseint all these things in sigma tropic. You have group transfer reactions, kelio tropic reactions where you study with your sulfur oxides reactions and then the two other minor which you can think about which your ene and retro ene. See, some people put your ene and retro ene inside your group transfer reactions but, they they have a separate class ene and retro ene reactions which you can study; another is your coarctate reactions.

Basically, that means we have to study this seven type of reactions. What we will be doing is that we will be spending time on each segment of reactions where you study in detail. You start sigma tropic we study in detail all the reactions involved in that. Then, we will move one by one and finish it off. These are the sound reactions which we are going to see in just coming classes. These are the classification see there are some methods by which you understand or you analyze pericyclic reactions by theoretically or by using orbital pictures, right.

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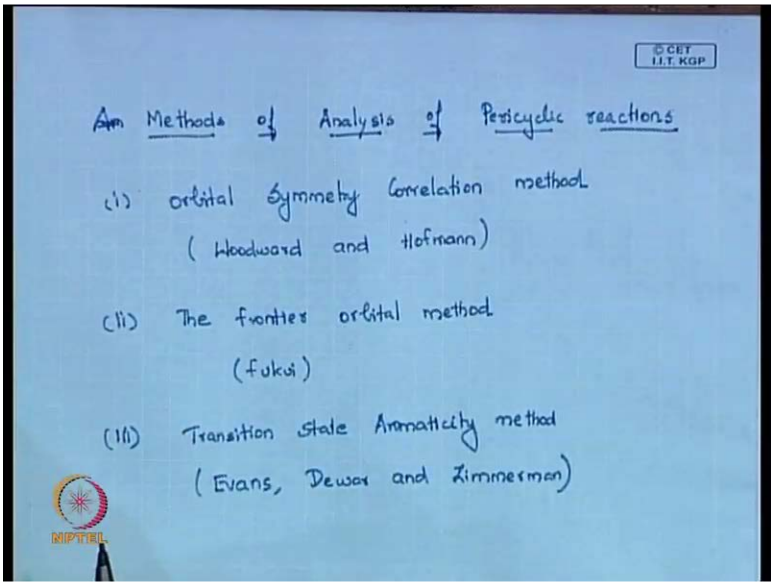

Am Methods of Analysis of Pericyclic reactions

(i) orbital Symmetry Correlation method
(Woodward and Hofmann)

(ii) The frontier orbital method
(fukui)

(iii) Transition State Aromaticity method
(Evans, Dewar and Zimmerman)

There are three methods by which you methods of three methods you use to understand pericyclic reactions. One is your study this orbital symmetry correlation method; any idea who did this? And, other Woodward and Hofmann their contribution, was great on orbital Woodward and Hofmann, of course, orbital symmetry than any other which you remember mobious; very good that its totally another is this the frontier orbital method, right; this very important one. Frontier orbital f m o which uses this molecule orbital theory done by Fukui right; this mobious all this comes under this theory transition state aromaticity method. But, actually this is started by you are in a ( ) start would you major contribution on this big names Evans Dewar and Zimmerman. It is better to know that people who are contributing on these particular areas any chemistry if you take you better know the people who contribute.

So, you can use these 3 metals like orbital’s symmetry correlation f m o and your transition state or aromaticity to understand your pericyclic reactions before getting in detail pericyclic reaction. Just I know that you guys know about all these things. I want to just brush your molecular orbital picture, just for ethylene butadiene or cyclo heptatriene just brush it because, I know that you have studied in detail in other courses just have a re-brush.

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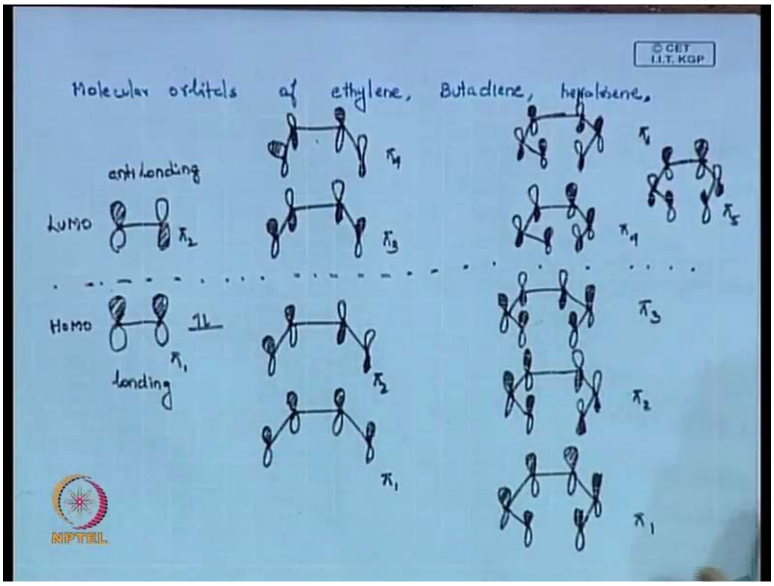

Just see molecular orbital's of ethylene butadiene heptatriene; see ethylene is you guys have studied it is not heptatriene; sorry, hexa right hexatriene. So, you know ethylene if I say it bonding and should be this one and it should be the HOMO right highest occuphid molecular orbital. This should be your anti bonding side and this will be your LUMO. If you see the face of ethylene is you get this phase right which you have studied and in anti bonding it will be reverse of it. You can build your butadiene based on this right you can call this as phi, 1 and phi 2. See, I want you guys to at least draw this you have studied it is fine but,…

You can take your ethylene; you can have this combination same phase combination then you can get this ethylene with the same face or you can have the face in the different way then, you get the down word right. You can build up our… so it is phi 1 and phi 2 simply you can make this simple. You can combine these two phases like this is one then you can take this face and combine.

One other this will be always see the easy right phi 3 and phi 4 nice; so, slowly you can build up like this. If you want to draw hexatriene can you draw hexatriene like treine hexatriene system there you have like. See when we see book we just visually we see that and we leave it can you draw it is nice so what you do how you build up this system you can take this bonding with phi 1 you end up this phi 1 system, you can take this bonding and you can do with you phi 2 end up with phi 3 right.

Mix these 2, you end up phi 1; mix these 2 you end up phi 3; that is how you build up. So, if I just build up so this all will be in the same phase because of this two mixing if mix phi 1 of my ethylene and phi 2 of butadiene. You just see that I get my phi 3 the phi 2 system mostly have this type of nodes of symmetrical which you have studied; so which will be like 3 phases will be up and your 3 phases will be down of your phi 2.

If you keep like this that is, how you build up your phi 2, phi 1, phi 2, phi 3? Now, can you draw for your phi 4, phi 5, phi 6? Same idea; so, once you know then it is nice after this you can get into your pericyclic. I know that you guys know it but, just I can say this my phi 4 where you have this combinations right down, now I have down up then I take this one and this 1, this phi 4. Then, I can have this combinations this will be phi 6 I will draw the phi 4 but, this phi 6 meet. because it is a major you are going to talk and your phi 6 phi 5 since I do not have space I am drawing that also have a type of where you have an this type of symmetry. Same way down and down that is your phi 5. So, you can just by combining, you can build up your systems. It does not need that you have to memorize all these things; just by two combinations. How to combine and just slowly you can build up ethylene butadiene treine systems etc I hope that you can do even for octal tetrine you can build it up; so that is fine about your molecular orbital. What we are going to learn from this? What it going to tell you when you have a pericyclic reactions, what it tells you basically?

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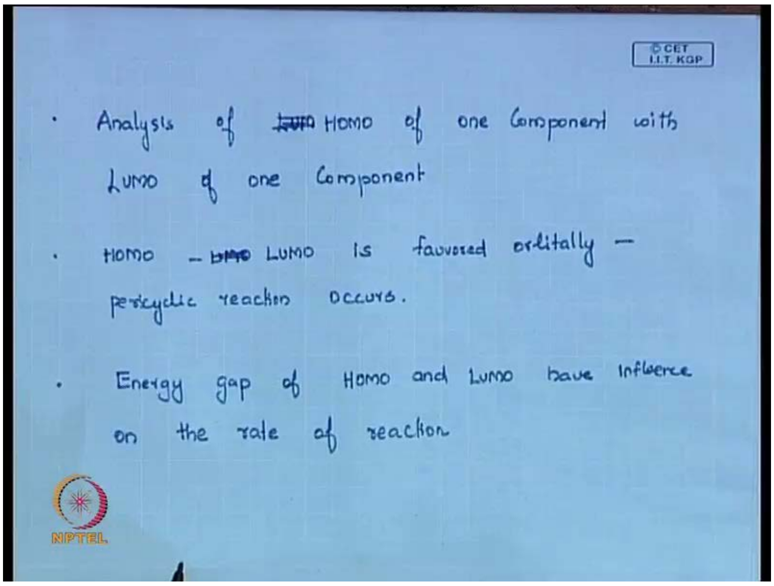

- Analysis of ~~[illegible]~~ HOMO of one Component with LUMO of one Component
- HOMO – ~~[illegible]~~ LUMO is favoured orbitally – pericyclic reaction occurs.
- Energy gap of HOMO and LUMO have influence on the rate of reaction

See when you want to analyze a pericyclic reaction, first point is that you analyze analysis of basically, sorry, HOMO of one component with LUMO of another component; that is two you use whenever you see your immediately, when you see a reaction you consider the HOMO and the LUMO and see whether if HOMO and LUMO are favored. That means, their phases are same which you which in detail I will tell you the HOMO and LUMO is favored orbit ally. I will explain in detail what is favored orbit ally then you say the pericyclic reaction proceeds.

That you can understand the third point; you can understand that the energy gap of HOMO and LUMO have influence on the rate of the reaction, what is the Radom? You see that the energy gap between your HOMO and LUMO, once very small the reaction process very fast. So, these are the three things which you can understand by seeing your orbital when you are given a pericyclic reaction. Please see the HOMO and LUMO of both the components and see whether they are orbit ally favored if they are orbitally favored reactions, goes the gap is very small then the reaction process very fast.

Now, we will get this is the broad introduction of your pericyclic reactions. Now, we will take individual reactions and see in detail since you guys have studied the energy gap of your HOMO and LUMO have influence on the rate of the reactions.

I know that the undergraduates are where you have studied more in detail about electro cyclic reactions. You have studied also something about your cyclo additions; not seen you guys study sigma tropic reactions in detail. Just have a glance; what I thought like I will first take sigma tropic reactions we study in detail. Anyhow, you can cover this all cyclo additions and electro cyclic but, I thought first I will concentrate on sigma tropic then we will move slowly from there.

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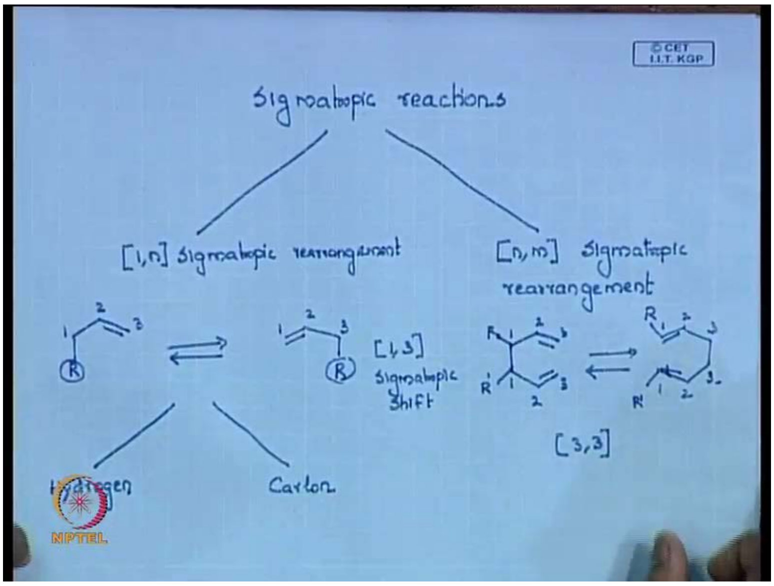

To start with reactions we will start our sigma tropic reactions. See, sigma tropic reactions bill are broadly classified into two groups. One you call them as 1 coma n sigma tropic rearrangement; another you can call them as n coma m sigma tropic rearrangement. That is how you can broadly classify what is basically coma n we are talking about. So, if I have reaction I just say this R is a residue; once I heat this reaction and number it 1 2 3 this one stands for the initial position of your R. What happens then? You get a product like this. Now, this residual has moved across the phi system and based your position like 3. In this case, that is your n, so it can be called as then 1 coma 3 sigma tropic shift; that is how you call them: 1 coma 3 sigma tropic. Shift ( ) in this 1 coma 3 1 is your initial where the R is that you always number as 1 and then where it as finally, moved that you call as the end it can be 3 5 7. Whatever it is see in sigma this R most of the time you are going to discuss 2 1. You are going to discuss hydrogen you call them. Then, 1 coma 3 hydrogen shift if the R is hydrogen or you discuss with your carbon this are most you see either you see an hydrogen shift or you see a carbon shift or it is metal or whatever carbon shift, right.

These are the 2 big classes of your one end; so sigma tropic classified as 1 n and n coma m and in 1 n. I can further classify the ( ) 1 coma n hydrogen shifts as well as 1 coma n carbon shift. So, what is this n coma m have system 1 2 3 1 2 3? So, in this case if you see it is your sigma bond has been moved across your phi system. So, initially your sigma bond which is doing the reaction that you cal as 1 1 and where it has finally reached. In this case it as went to 3 in 1 side and another side also it went to 3 what all want to say so this is then what system it is n is 3 your m is also 3 in this case so you call it as 3 coma 3 there are but, there are many examples of 2 coma 3, any example of 2 come 3 which you know. 2 coma 3 reactions add numbers 1 coma 2 ( ) is 3 coma 3 5 coma 1 coma. You have all your elide chemistry sulfur elides, all your elide chemistries goes by 2 coma 3 is sigma tropic shift. We will see that there are many, so you have to find out where the new bond is moved. I H m in this case it is 3 and 3; so, your n is 3 and m is 3 if you just 2 and 3 it becomes 2 coma 3 sigma tropic shift. So, these are the two parts which you are going to study sigma tropic first. We will be discussing about hydrogen shift in detail then we will move to carbon 1 coma n carbon and then we will study n coma m sigma tropic shift clear.

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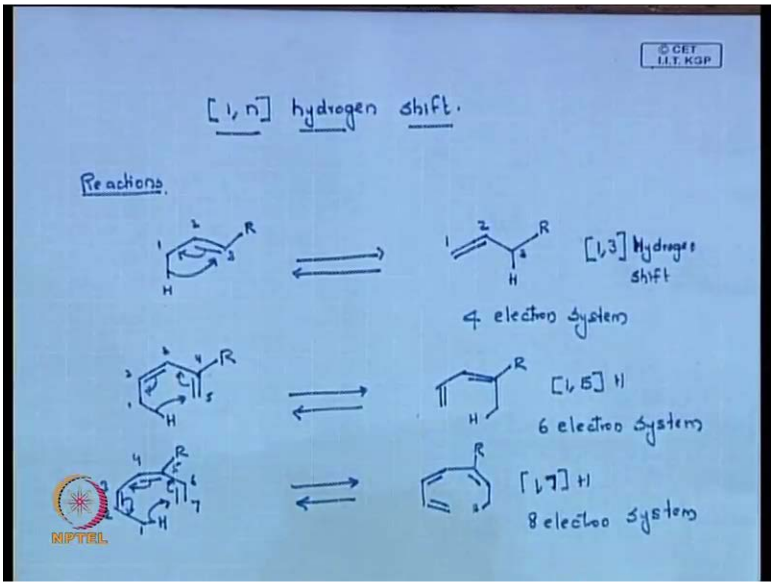

We will start then with 1 coma n hydrogen shift. First, we will see the simple reactions very simple general reactions and then we go in simple reactions like just what I have said. Now, see when you write pericyclic reaction, you write both the ways because it can happen. So, I number it 1 2 3; see the electron push because, that is how you represent that you just write 1 coma 3 you can write hydrogen shift small H in this back 1 coma 3 hydrogen shift; all people write 1 coma 3 like hydrogen H.

Way of writing it now it is different from your heliport cyclic when you count the phi system 4 n rules and 4 n plus rules which you do in electro cyclic in this case it is little bit different. What you do is that you consider how many electrons are there involved in this reaction that is how you can see that see 2 phi electrons as well as 2 sigma electrons so you have now 4 electrons system.

Basically, this is 4 electron system some where you get loss when you go to electro cyclic and this just you see the electro cyclic system here you have to see the phi system and your sigma system so you see now it is as a 4 electron system when you apply your Woodward Hofmann rule; then you apply with this electron.

So this will be your 1 2 3 4 5, so this will be your 1 5 hydrogen shift and basically, it will be 6 electron system that and one more which we will be discussing. So 1 2 3 4 5 6 7, so it is 1 7 hydrogen shift; so its 8 electron system, right. A reaction wise now you know how to number it and how to represent these guys and how much electron system, it is involved right any doubt on this. Now, I will bring a small additional point into this reaction that is if I take a system this is very simple.

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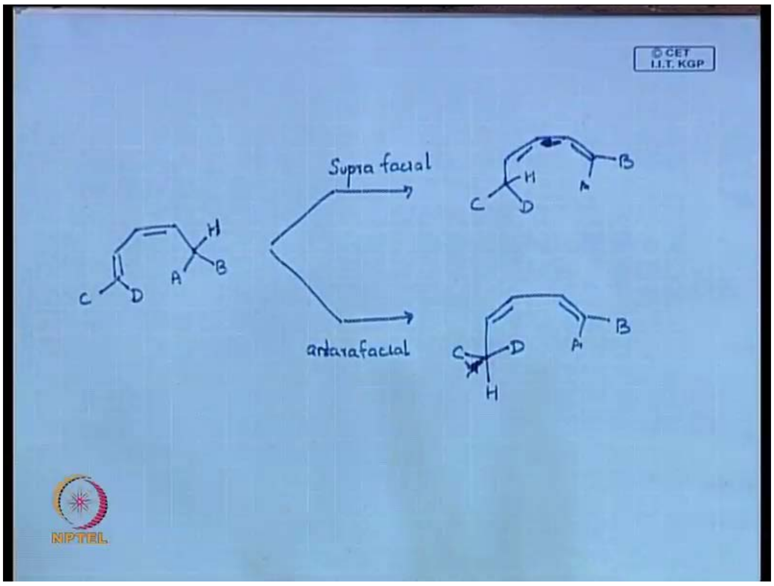

You just remember if I take a system like this general representation, this is your hydrogen. Now, if you know if I heat this reaction it will happen what 0.5 but, once your hydrogen moves to C and D. It will going to generate a type of carol carbon then this steroid chemistry comes into picture right so it can be two way one it can be R or it can be S right where if I. Sorry sorry sorry oh you will C can like this mark anything. So, you have A C D hydrogen and this now in one case if you see your hydrogen as went with the same phase. Another case if you see the hydrogen as you went down na opposite phase right it as some sort of inversion as been taken place in one case it as na same phase so that you call as supra facial where your hydrogen went in the same phase without disturbing another case you call them as an antarafacial see slowly bringing a steroid chemistry in this shift that is how first you know how to do your hydrogen shifts you know what is 1 3 1 5 1 7 even how to label them how to push your electrons how many electrons are involved.

Now I am bringing one more concept of steroid chemistry if your hydrogen moves without changing the phase then you say supra facially if there is an inversion then you say antarafacial clear you can you can visualize this even with orbital's I will just show how you can see this in an orbital way.

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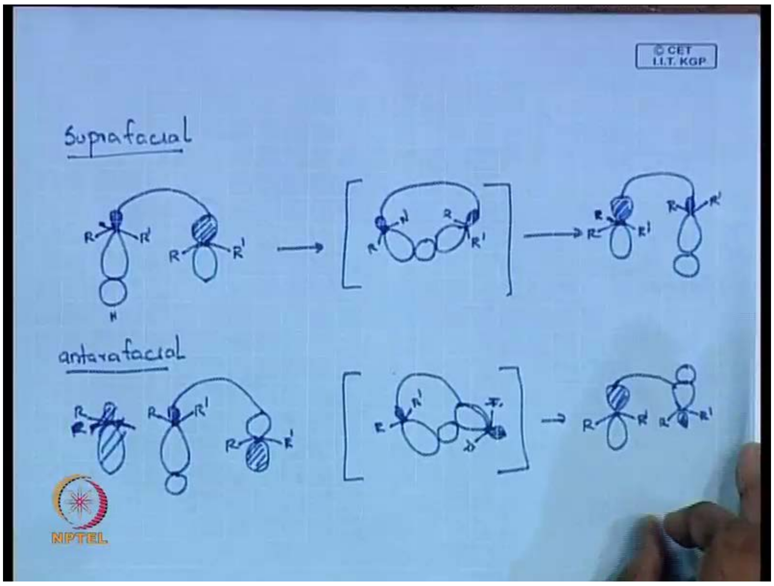

If I want to draw supra facial see you may have R and R prime and this is my hydrogen which I am talking about and this if you want to think about supra facial one how you stage should look see your R R prime this are moved like this so it will be R R prime then basically it can reward back giving this so this can become now without your hydrogen can have a system of yeah if it is yeah it is nice that you R R prime then you have this one which you be having small, right. So, supra facial looks to be easy to draw back just cause a data on that R and R prime also, that also tells like what phase it goes on. Can you draw now antarafacial idea, can I will just give you the picture?

Ok, most of the time if this R should be in the… have an hydrogen here, see antarafacial means your orbital will be in opposite thing. Now, you can think how to draw this in thing this way, you how the antarafacial looks, how these guys can.

Now, I want your R this R prime to be because it as turn like this, right? So, your R prime will be on this and your R will be here, right. I just turn this; now it just because right see I think when you move across you keep R and R prime understanding because, that will guide you and even I have seen people drawing like even if this hydrogen nucleus this will be big and symmetrical. It does not work like that when you have hydrogen system you have smaller ( ) across that you have studied it. So, that is how you can visualize your supra facial and antarafacial by orbital if you know what. So, based on this orbital picture Woodward and Hofmann formulated a type of rule right finish.

This interaction, see this one, see I want to take this up this line you are talking about. It should be in this because, it this is connected this is only to say that it is connected. So, hence it is an, I am talking about any phase in this line connected, just a bond system not the phase I am not talking about phase; that is good.

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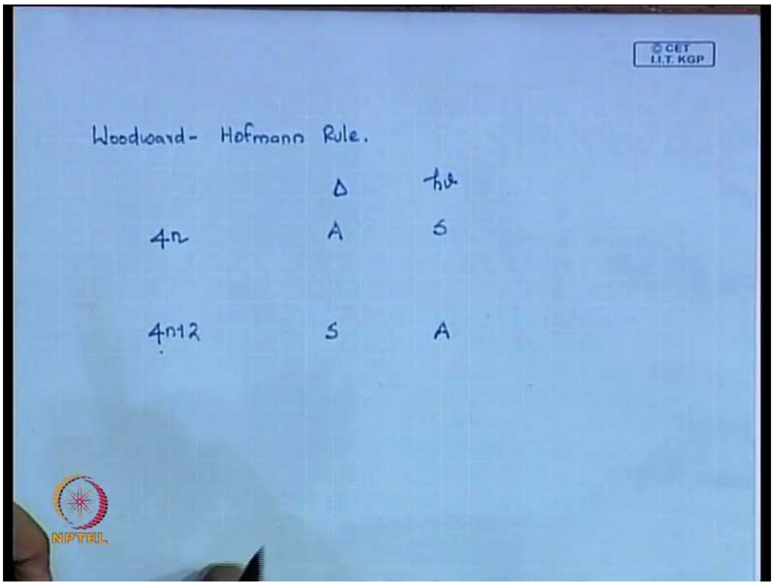

Woodward- Hofmann Rule.

	Δ	$h\nu$
4n	A	S
4n+2	S	A

So, what your Woodward Hofmann rule says about the system type for one end system? if you have a 4 end system I am talking about the electrons 4 n and 4 n plus 2 electrons where you fit in; so you have a heating and you have a proteolysis case.

So, 4 n system basically on heating is your antarafacial and light it should be always on other ways on supra facial - this is supra facial - and this is your antarafacial. That means, what I say is that, what is your 1 5 1 5 is 6 electron system, right? 6 electron system will fit in this rule 4 n plus 2. Then, it is supra facial heating when it slants light it will be antarafacial. So, like that you can fit your rules; so it exactly works only one case; it does not work, this one it is your 1 3 shift main so one thing you have to learn about your 1 3 hydrogen shift, fine.

So what I will do? In that exceptional case or that 1 3 hydrogen shift, we will see in next class. I will teach you why it does not fit in; it fits but, you guys know that 1 3 hydrogen shift on heating does not take place. If you heat you cannot see most of the time you cannot observe any 1 3 hydrogen shift that will see in next class why it is not happening. Then, we will see you 1 3 carbon shift and we will do the problems; then we will move to your n coma m we will stop the class with this.