Symmetry, Stereochemistry And Application
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Lecture No-45
Name Reactions and their Mechanism - Part 02

Welcome back to the course entitled symmetric stereochemistry and applications. We are in the 10th week now and in the previous lecture we were talking about the stereochemical aspects of Diels-Alder reaction.

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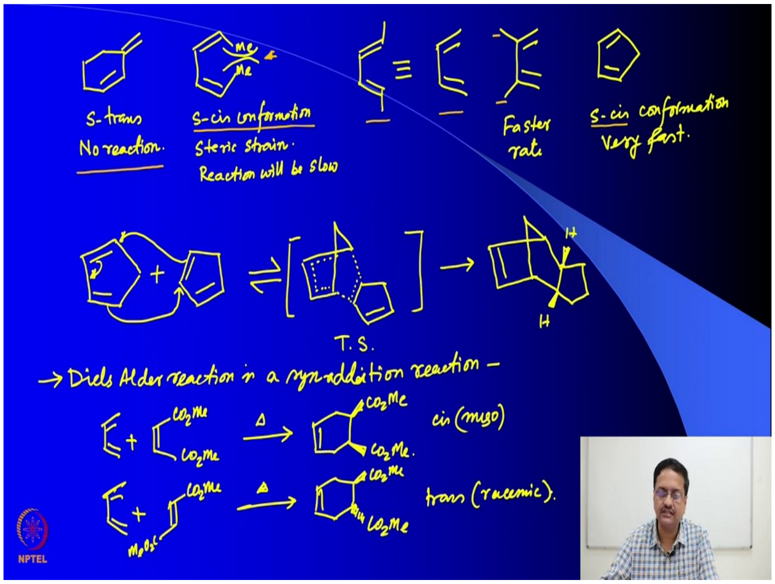

So, I will continue from the last slide where we left in the previous lecture. So, we discussed about the rate of reaction of various dienes and we indicated that the compound with always S-trans conformation will not undergo any Diels-Alder reaction the compound which can go for has s- Cis conformation but has a steric factor involved in it will go for Diels-Alder reaction but the reaction will be extremely slow.

And then we have two standard dienes which will have moderate reaction rate and when we add more electron donating groups on the diene in suitable positions then the reaction becomes faster and the compounds which always have s-cis conformation the reaction will go in a very fast pace. So, when I was discussing about this cyclopentadiene, this cyclopentadiene efficiently undergoes self dimerization through Diels-Alder reaction.

And this happens even at room temperature and then you always end up getting the dimer of this product. So, the reaction as usual happens in a concerted step and it forms a cyclic intermediate or cyclic transition state not an intermediate it is a transition state. These dotted lines are the bonds that are forming or breaking in the molecule. So, this is the cyclic transition state for this reaction and eventually we get a product which is this one.

So, this is called the self dimerization of cyclopentadiene. This Diels-Alder reaction is a syn addition reaction which means that it maintains the stereo chemistry of the reactants. So, if we treat cyclobutadiene with the Cis diester we would get a product where the diester will be Cis and if we use the same butadiene with the trans diester under the same conditions of heat the product that you would get would be a trans ester and this cis compound is a meso compound and the trans appears as a racemic.

So, Diels-Alder reaction is a syn addition it maintains this stereochemistry of the reagent or the reactants in the product and it does not it here it does not generate one particular isomer rather it generates the racemic modification of this compound.

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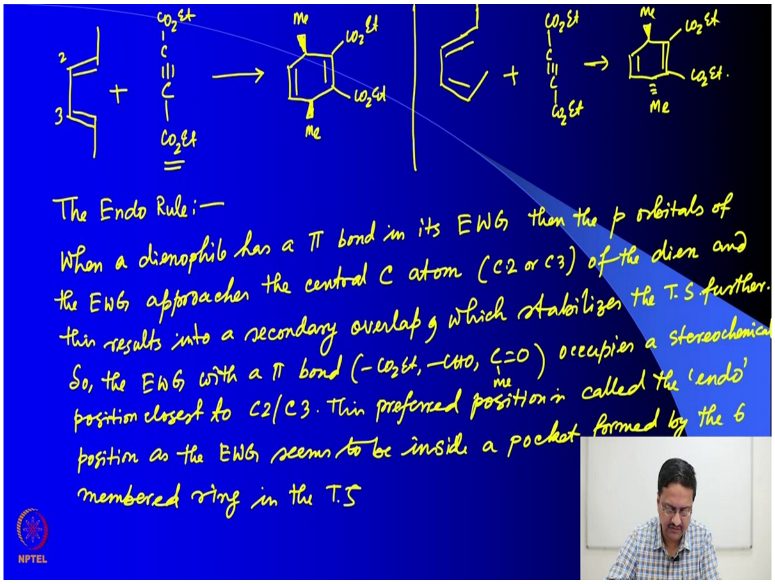

The Endo Rule:—
When a dienophile has a π bond in its EWG then the p orbitals of
the EWG approaches the central C atom (C2 or C3) of the dien and
this results into a secondary overlap g which stabilizes the T.S further.
So, the EWG with a π bond (−CO₂Et, −CHO, $\underset{me}{C}=O$) occupies a stereochemical
position closest to C2/C3. This preferred position is called the 'endo'
position as the EWG seems to be inside a pocket formed by the 6
membered ring in the T.S

So, let us take two more examples. So, when you start with this compound where the two methyl groups are on same side that means this opposite to each other the in the product they would appear as cis. If you do the reaction with the butadiene where the methyl groups one is outward and the other one is inward which means here it is trans and there it is cis and you treat it with the same dienophile the product that you would get is a trans compound with respect to the methyl groups.

So, this ensures the syn addition of the compounds in Diels-Alder reaction. So, now let us talk about another rule which is called the Endo rule. This rule is applied when a dienophile has a pi bond in its electron withdrawing group just like here then the p-orbitals of the electron withdrawing group approaches the central carbon atom that is either C2 or C3 if I name it as 2 and 3 for a butadiene C2, C3 of the diene and this results into a secondary overlap which stabilizes the transition state further.

So, the electron withdrawing group with a pi bond the group may be CO2Et CHO COMe whatever it may be occupies a stereochemical position closest to C2 or C3, this preferred position is called Endo position, as the EWG the electron withdrawing group seems to be inside a pocket formed by the 6 membered ring in the transition state.

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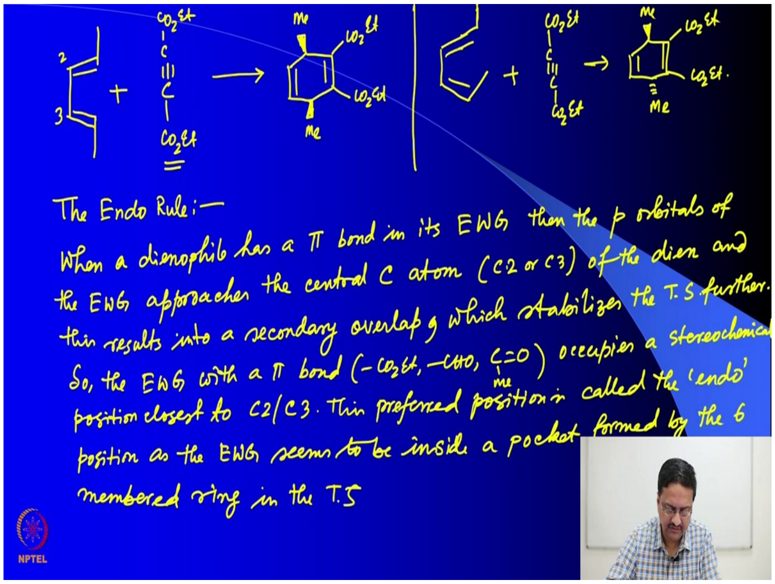

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So, the EWG with a π bond (–CO_2Et, –CHO, $\underset{Me}{C}=O$) occupies a stereochemical position closest to C2/C3. This preferred position is called the 'endo' position as the EWG seems to be inside a pocket formed by the 6 membered ring in the T.S

So, let us try to understand what exactly is meant by this. So, when you have a compound which is this one, the cyclopentadiene and you are treating it with the aldehyde here like this. So, the product would be like this, this is the endo position and this is called the exo position. In a 3 dimensional view this would look like this. So, as if the location of this CHO is closer to the C2 C3 carbon atom and this is called the Endo rule.

So, let us try to use that Endo rule and understand how Diels-Alder reaction can yield various different products and what will be its stereo chemistry. So, for example if we use this cyclopentadiene and treat this with this anhydride, the product that would form should be drawn like this. The hydrogens are up, double bonded O and single bonded O which is here and this methyl groups this carbon which is connected as a bridge head.

So, this group which is hanging below is hanging at the endo position with respect to the point where the new bonds got formed. So, if we try to see it with a different reaction, propenal, So, this reaction will proceed in the same way. But it will generate a product which will have the CHO group closer to this pi bond and the hydrogens away right. So, this is the endo compound, the other possible compound would have been this one.

So, this is called the exo product which does not form, the endo product forms as a major product, exo product may form in some cases as a very, very stress quantity. So, this Endo rule actually predicts what should be the major product of a particular Diels Alder reaction. So, I would like to give you a homework to draw the product of this particular reaction, what is the product of this particular Diels Alder reaction you try to identify at your home.

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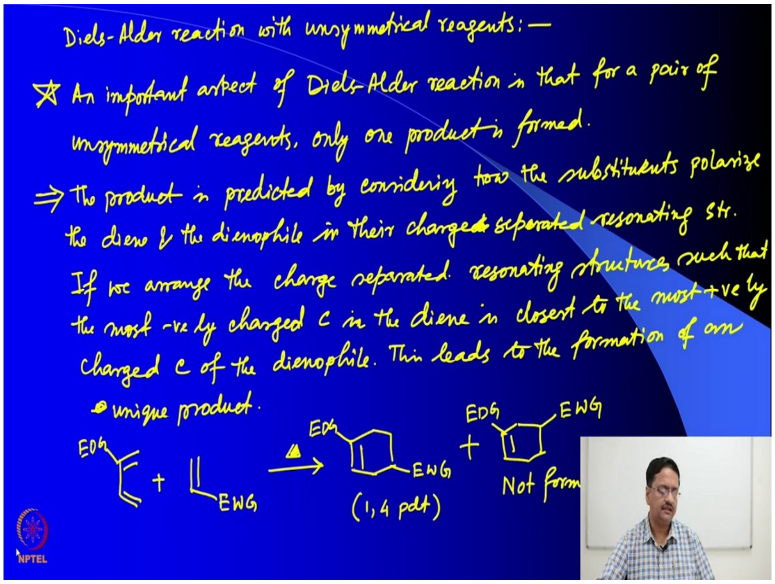

Diels-Alder reaction with unsymmetrical reagents:—

☆ An important aspect of Diels-Alder reaction is that for a pair of unsymmetrical reagents, only one product is formed.

⇒ The product is predicted by considering how the substituents polarize the diene & the dienophile in their charged separated resonating str. If we arrange the charge separated resonating structures such that the most -vely charged C in the diene is closest to the most +vely charged C of the dienophile. This leads to the formation of an unique product.

We would like to discuss some other aspects of Diels-Alder reaction, the first thing that we would like to discuss what happens if we do a Diels-Alder reaction with unsymmetrical substitutions or unsymmetrical reagents and important aspect of Diels-Alder reaction is that for a pair of unsymmetrical reagents only one product is formed. The product is predicted by considering how the substituents polarize the diene and the dienophile in their charge separated resonating structure.

If we arrange the charge resonating structures such that the most negatively charged carbon in the diene is closest to the most positively charged carbon of the dienophile, this leads to the formation of an unique product. So, if you have if you have an electron donating group on the diene and an electron withdrawing group on the dienophile and it makes these two compounds as unsymmetrical.

Although there are possibility of two products the product that is formed is this one, one four product, other product which does not form.

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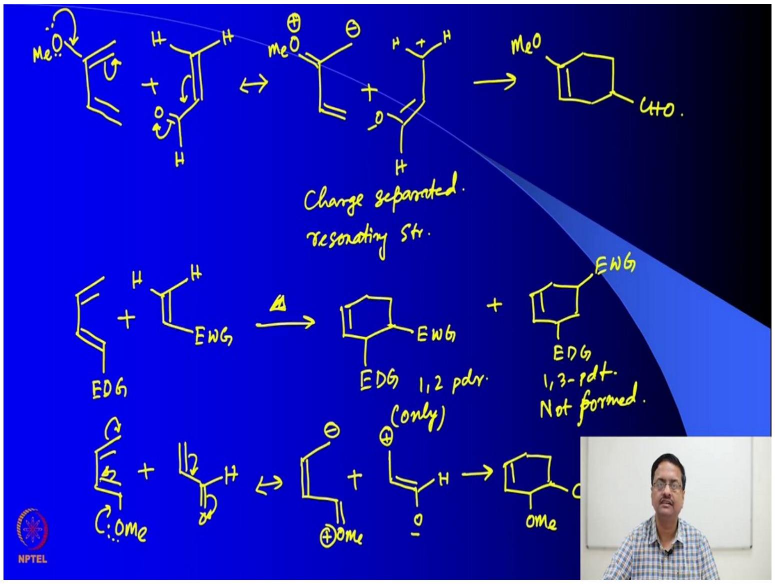

So, as a real example one can think of a reaction like this. The charge separated resonating structure of this molecule would look like this. So, as a result the reaction will take place in this particular orientation and what you would get is the product which is this one as the only product. On the other hand in case of a different combination of the diene and dienophile when the electron donating group is on the carbon number one.

And the electron withdrawing group is also present in the dienophile, then on heating what you would get is a one two product not the other one. The other product that is possible is the corresponding one three product which does not form, not formed. So, if you try to draw the charge separated structure for this type of compounds where you may have a methoxy group present and you have an aldehyde group present on the dienophile then the charge separated resonating structure would look like this.

So, as a result the product that would form out of this reaction is this one. So, this is how we can think of doing a Diels-Alder reaction using some unsymmetrical diene and unsymmetrical dienophile. So, from here we will continue in the next lecture, thank you.