Symmetry, Stereochemistry And Application

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Lecture No-44
Name Reactions & Their Mechanism - Part 01

Welcome back to the course on symmetry stereochemistry and applications. This is the 10th week of this course. So, in this course now, in this week we will discuss about a few well known chemical reactions and we will discuss about the reaction mechanisms of those reactions. So, today in the first lecture I am going to start discussing about the well known Diels-Alder reaction.

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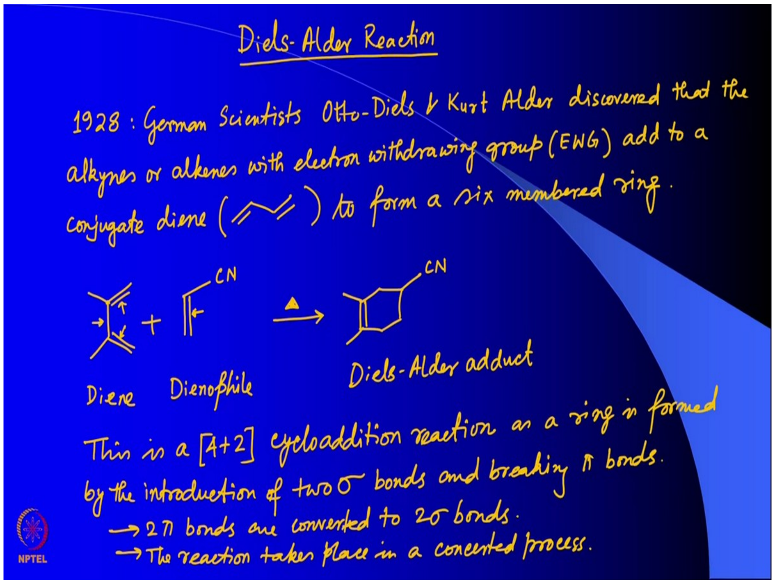

Diels-Alder Reaction

1928 : German Scientists Otto-Diels & Kurt Alder discovered that the alkynes or alkenes with electron withdrawing group (EWG) add to a conjugate diene ( ) to form a six membered ring.

This is a [4+2] cycloaddition reaction as a ring is formed by the introduction of two σ bonds and breaking π bonds.
→ 2π bonds are converted to 2σ bonds.
→ The reaction takes place in a concerted process.

This reaction is known since 1928, German scientists Otto-diels and Kurt Alder discovered that the alkynes or alkenes with electron withdrawing groups we write it as EWG add to a conjugate diene that is a compound which has 2 consecutive double bonds like this to form a 6 membered ring. So, the reaction that they proposed or that they discovered is the following, when you have a diene like this we have 2 double bonds a conjugate diene is treated with a double bonded compound with an electron withdrawing group connected to it.

So, this compound is called dienophile which means a diene loving substance. So, when you heat these 2 compounds what happens is we get a cyclic product as I am drawing here this product is called the Diels-Alder Adduct. So, this particular reaction is also called a 4 plus 2 cyclo addition reaction, this is a 4 plus 2 cyclo addition reaction as a ring is formed by the introduction of 2 sigma bonds and breaking pi bonds 2 pi bonds rather or rather 3 pi bonds.

So, now what happens is 2 pi bonds are converted to 2 sigma bonds and the reaction takes place in a concerted process, which means the breaking of the pi bonds and the formation of the sigma bond takes place simultaneously. So, what we are seeing here is that the pi bonds that are being broken are those 3 and a new pi bond is formed here in the CC bond in between the diene molecule and 2 sigma bonds are formed here 2 new sigma bonds are formed 3 pi bonds are broken.

So, technically 2 pi bonds are converted to 2 sigma bonds and what is the important aspect here, the important aspect is that the reaction proceeds with a dienophile which has an electron withdrawing group.

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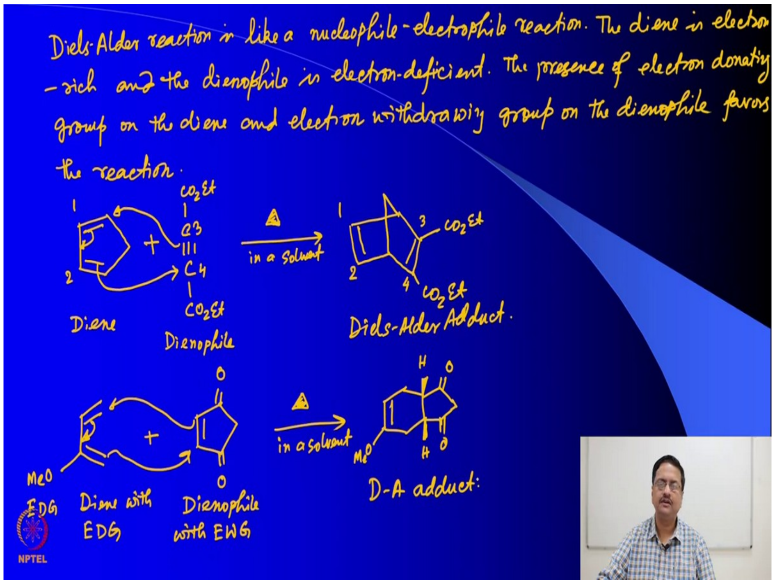

Diels-Alder reaction is like a nucleophile-electrophile reaction. The diene is electro
-rich and the dienophile is electron-deficient. The presence of electron donating group on the diene and electron withdrawing group on the dienophile favors the reaction.

So, this Diels-Alder reactions is like a nucleophile electrophile reaction. Here the diene is electron rich and the dienophile is electron deficient, the presence of electron donating group on the diene and electron withdrawing group on the dienophile favours the reaction. So, Let us see this with a few examples, suppose we have cyclopentadiene and we are treating this with a compound which has a CC triple bond and has the ester group on each of those carbons connected to the triple bond.

So, the cyclopentadiene is called the diene here and this diester is called the dienophile. So when we heat these 2 compounds in a solvent what we get is a reaction in which the bond migration happens like that and what we end up getting is a compound which is this one. So, here this was our 1 and 2 and that 1 and 2 are here and 3 and 4 are those 2 which are here. So, this is called the Diels-Alder Adduct. So, similarly if we have a diene which has methoxy group which is the electron donating group or EDG.

So, this is a diene with electron donating group and you have this cyclic diene cyclopentenedione which is a dienophile with electron withdrawing groups attached to it then a similar reaction can take place and a new compound will be formed on heating it in a solvent. So, the product that you would get is this one. Right.

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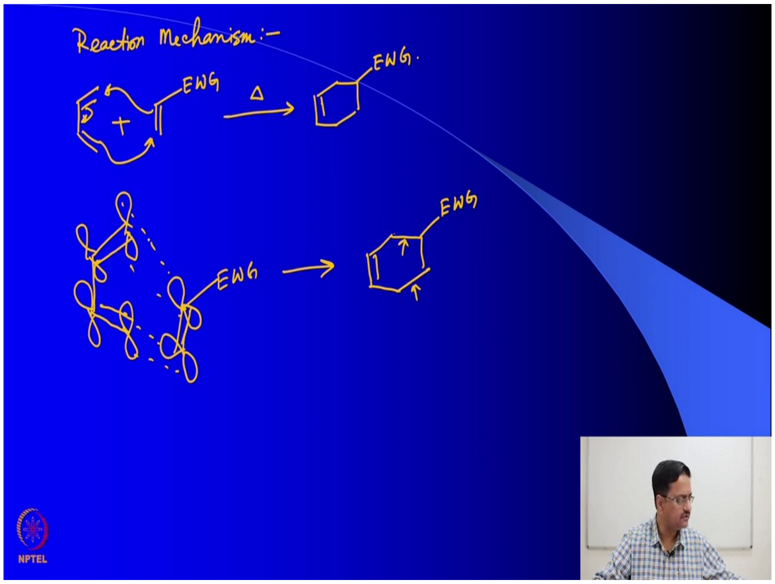

Reaction Mechanism:-

So, this is the Diels-Alder adduct. So, hope you can now follow what exactly means by a Diels-Alder reaction. So, now let us try to understand the reaction mechanism of this Diels-Alder reaction. So, as I already indicated using the arrows which indicates the movement of electrons, reaction happens in a concerted mechanism and a product is formed, an Adduct which is this is formed. So, what happens here is that the pi bond of the diene which is drawn here.

If I try to draw the p orbitals on that and the corresponding p orbitals dienophile they interact like this and they will form the product with a double bond being shifted and a new a pair of new sigma bonds formed between the overlap of these 2 molecules. So, now if we try to see some of the examples of Diels-Alder reaction some well known examples of Diels-Alder reactions, the

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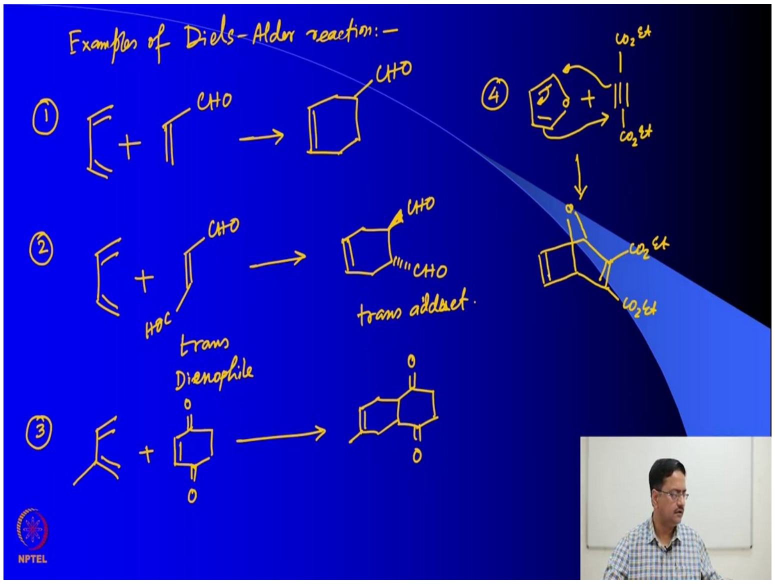

Examples of Diels-Alder reaction:-

Simplest one that one can think of is a butadiene reacting with butanal that means sorry ethenal which essentially gives you a simple product like this example number 2 this butadiene is reacting with sorry this is propional this trans diel is treated with 1 3 butadiene the product is only this one what does it mean the trans geometry in the dienophile is maintained in the product.

Which means this reaction maintains this stereochemistry of the substrate and does not allow any change in stereochemistry of the substrate which essentially indicates that this reaction happens in a concerted mechanism. Now if we have a diene with electron donating group on that, that is a methyl group and we are treating it with this diketone, cyclohexene diketone the product that we would get is this one.

So, similarly let us take the fourth example with this diene which is treated with a C triple bond C compound with CO2EtCO2Et on either side, the product of this reaction would be a bridged compound and that would look like this. So, these are some reactions which essentially indicates that this particular reaction that is Diels-Alder reaction is a concerted step.

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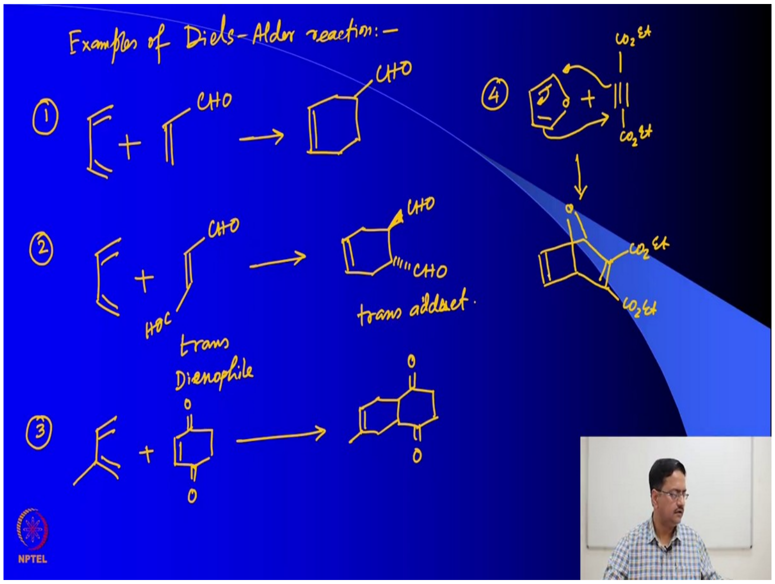

Examples of Diels-Alder reaction:-

And it gives you a cyclic compound as a final product. So, now the question is what is the stereo chemical requirement of Diels-Alder reactions? So, the first point that one should understand that it is a concerted mechanism through a cyclic movement of 6 electrons through a cyclic transition state, the transition state must have a geometry that allows for the overlap of p orbitals of diene with the p orbitals of the dienophile. What is the advantage, the concerted mechanism allows us to predict the correct product and for a suitable arrangement of diene and dienophile is required.

So, for the diene should have s-cis conformation which essentially means that there can be a butadiene with S-trans conformation this S-trans is in equilibrium or with the s-cis conformation with s-cis being the less stable conformer. So, this s-cis conformation is required for the Diels Alder reaction to take place. So, as I indicated in the previous slide that this s-cis conformation when reacts with the alkene or the dienophile the transition state that appears looks like this.

And the p orbitals are such that they can overlap efficiently. So, this stereochemistry is absolutely required for a successful Diels-Alder reaction to take place and that is why we should always heat the solution to bring the S-trans conformation in the solution and then the reaction takes place smoothly to give you the density of the product.

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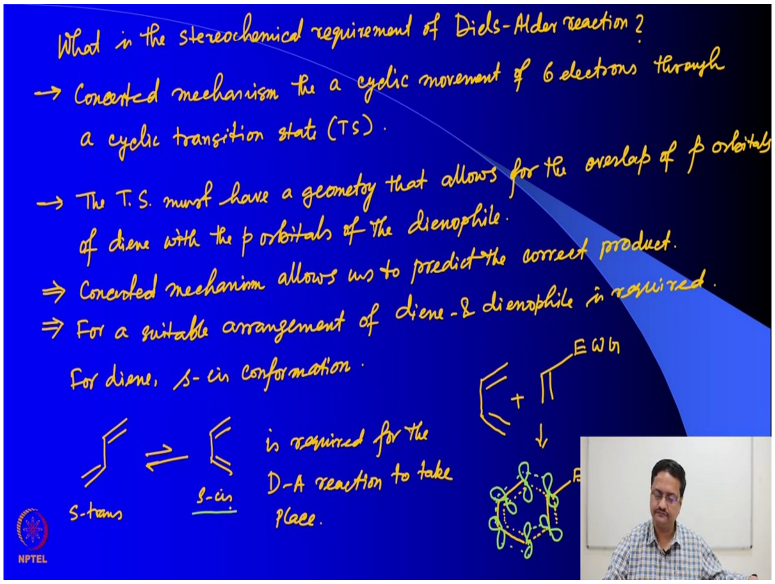

What in the stereochemical requirement of Diels-Alder reaction?

→ Concerted mechanism the a cyclic movement of 6 electrons through a cyclic transition state (TS).

→ The T.S. must have a geometry that allows for the overlap of p orbitals of diene with the p orbitals of the dienophile.

⇒ Concerted mechanism allows us to predict the correct product.

⇒ For a suitable arrangement of diene & dienophile in required.

For diene, s-cis conformation.

is required for the D-A reaction to take place.

So, when we try to draw a set of dienes. Let us see which of these dienes will undergo Diels-Alder reaction, see this particular diene has 2 double bond always in S-trans conformation and this does not undergo any Diels Alder reaction. If we take this butadiene with 2 methyl groups coming very close and having steric congestion this will have in case of s-cis conformation this will have steric strain.

So, the reaction will be slow, on the other hand if those 2 methyl groups were on the other side the reaction of that compound will be equivalent to 1 3 butadiene in its S-trans conformation then if we think of a diene which has 2 methyl groups connected on carbon number 2 and 3 this will have a faster rate of reaction and when we have a cyclic compound like cyclopentadiene where the conformation is always locked at s-cis conformation.

Then it is very fast which essentially means that this cyclopentadiene will always try to stay in its Diels-Alder Adduct condition and will not be available as a monomer in your reaction medium. So, from here we will continue in the next lecture thank you.