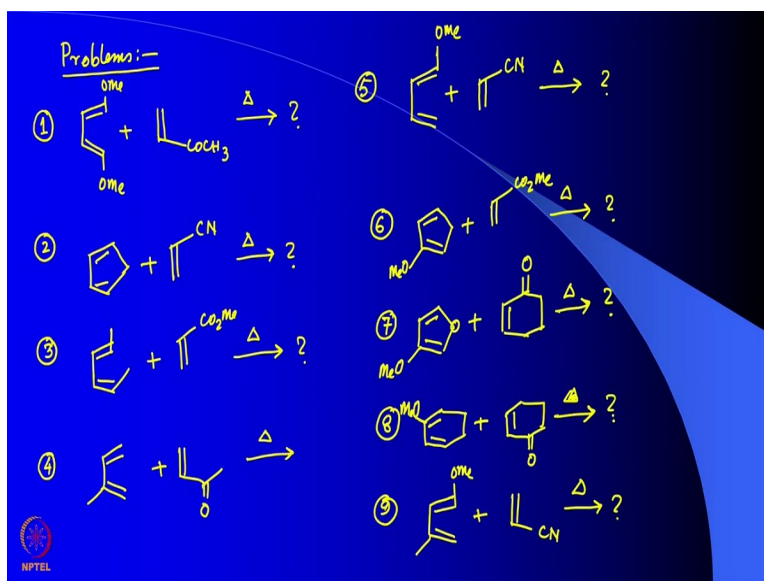


Symmetry, Stereochemistry And Application
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Lecture No-46
Modifications of Diels-Alder Reaction

Welcome back to the course entitled symmetric stereochemistry and applications. In this week in the first few lectures we have discussed about the Diels Alder reaction and its variations, its reaction mechanism and so on. So, in this lecture also I would like to continue discussing about Diels Alder reaction. So as you have already learnt a few aspects of Diels Alder reaction I would like to discuss some of the problems that you may find in your textbook.

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First I will write down the possible problems that you should try to solve and then slowly we can try to solve one or two in the later part of this class. So, here you have a symmetrically substituted diene with unsymmetrically substituted dienophile and this reaction I hope is very easy for you to guess the product because there is only one product and then there is only one way that you can think of and make the product and there will not be any difference arising out of the time.

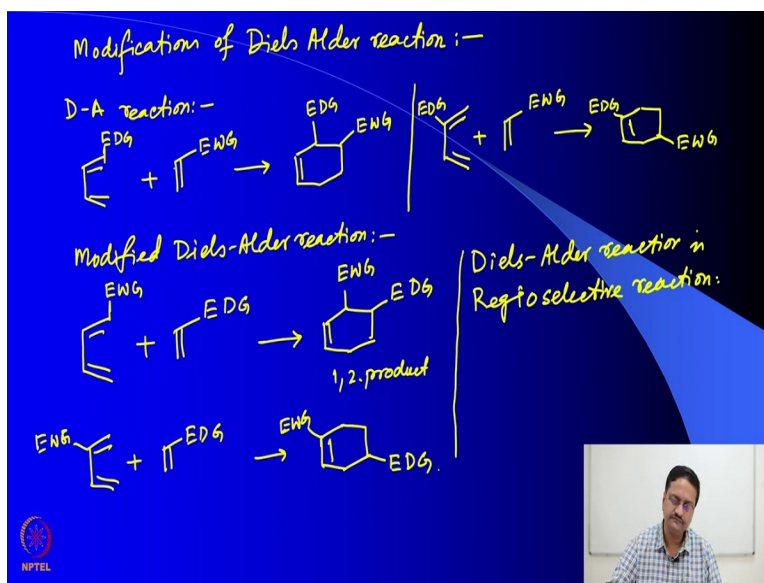
The second problem that I would like you to try to solve is this one. These are very simple Diels Alder reactions that I am drawing at the moment. Now here I am writing a few reactions where

you have the unsymmetrical substitution of on the diene or/and unsymmetrical substitution of the dienophile as well. Remember that all these reactions take place under heating conditions one can heat the reactants if they are liquid together without a solvent.

One can heat these reactants in a high boiling solvent by dissolving the compound in that solvent. You can see that I am slowly increasing the degree of difficulty and introducing the concept of Endo rule along with the unsymmetrically substituted diene and dienophiles. So, you should keep in mind that whatever has been discussed in first two lectures will be highly useful to solve these problems because these are the combination of everything that has been discussed in the previous couple of lectures.

So, I am giving you nine problems to work on yourself and we will discuss these problems towards the end of this week. So, let us try to see what are the possible modifications of Diels Alder reaction that one can think of?

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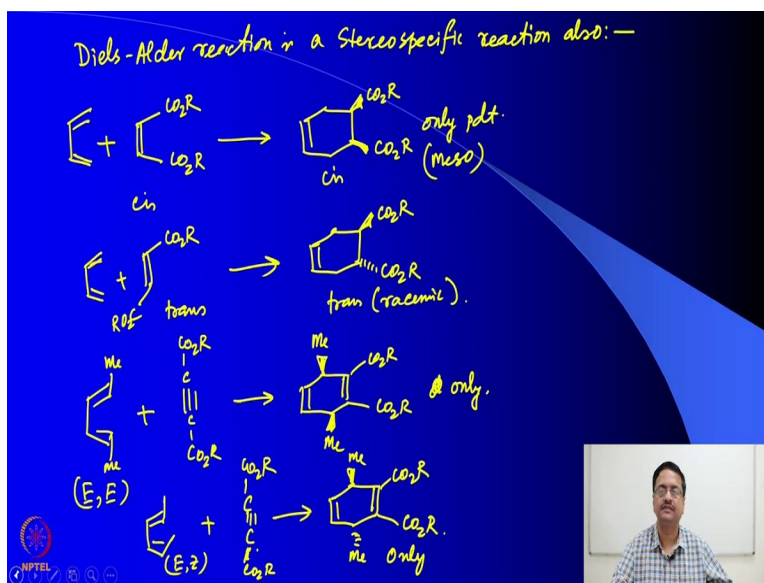
Modifications of Diels Alder reactions so, what we know about the standard Diels Alder reaction? We know that in case of a standard Diels Alder reaction we should have the electron donating group on the diene and you should have an electron withdrawing group in the dienophile which would give you a product. This particular combination would give you a product which is a one two product and the other combination where the the electron donating

group is at a different location with respect to the diene and electron withdrawing group is there as usual the product that you get is nothing but a 1,4 product.

So, if we do a modification of Diels Alder reaction and change the position of the electron withdrawing group and electron donating group and instead of having electron donating group on the diene we have electron withdrawing group on the diene and electron donating group on the dienophile. So, in that case when you have this condition that electron withdrawing group is on the carbon one and electron donating group is in the dienophile you would get a product which is the corresponding one two product.

And if you have the other possibility that the electron withdrawing group is on the carbon number two and electron donating group is there on the dienophile you would get the corresponding 1,4 product as was obtained in case of the actual Diels Alder reaction. So, this Diels Alder reaction is regioselective reaction. Among the two possible regions the reaction happens through a particular region only and not through the other region of the reactant and product sorry the diene and dienophile.

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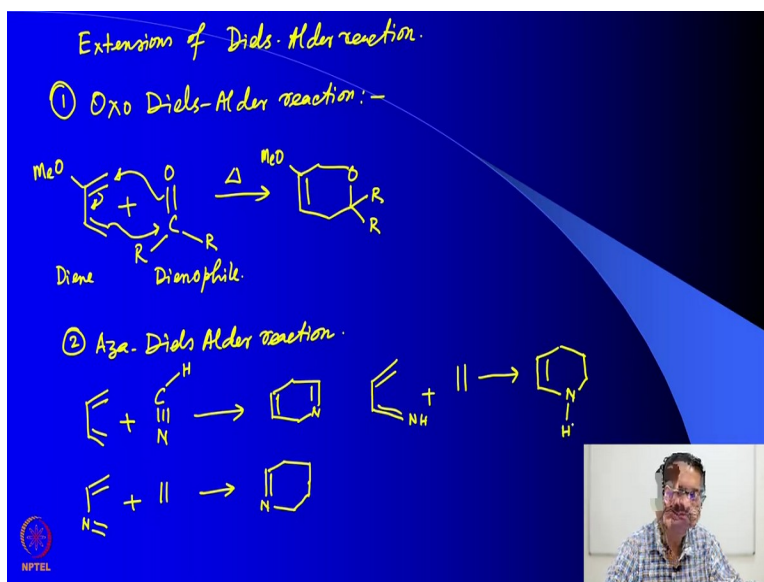


And we should also appreciate that Diels Alder reaction is a stereo specific reaction also how can we identify that? Suppose if we have a diene reacting with a *cis* dienophile. The product that forms maintain the *cis* geometry in the product if the same diene reacts with a *trans* dienophile

then we get the trans product only. Of course this cis product is a meso compound and this trans is a racemic mixture.

Similarly in case of diene when we have two methyl groups in the E, E configuration it reacts with a C-C triple bond with the ester group connected to the alkyne bond the E, E isomer gives rise to the cis compound. But if you take the corresponding E, Z compound and treat with the same alkyne one would generate the corresponding trans isomer. So, this is the only product. So, this clearly indicates that these Diels Alder reactions are highly stereo specific also. So, they are regioselective and stereospecific reactions.

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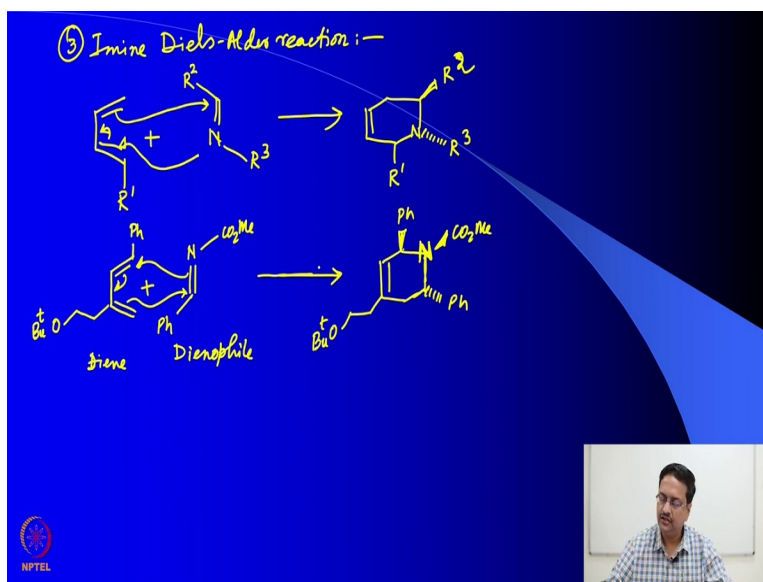
Let us try to see what are the extensions of Diels Alder reaction. So, the one extension is called the Oxo Diels Alder reaction. So, from the name itself you can understand that the cycloaddition reaction involves a carbonyl compound and C double bond O acts as the dienophile. So, one simple example of such Oxo Diels Alder reaction is this one, this 1,3-butadiene reacts with a ketone and gives you the heterocyclic 6 membered ring as I am drawing here.

So, this reaction is called the Oxo Diels Alder reaction where it involves the C double bond O in case as a dienophile. The second type of extension that has been done is called the Aza Diels Alder reaction. So, here a diene, is treated with a compound which contains C triple bond N

suppose HCN. So, in this simple reaction it forms a compound which has a nitrogen in the ring. So, similarly one can have a nitrogen in the diene.

Similarly one can have nitrogen in the diene and treat it with an alkene which is a dienophile and convert it into a heterocyclic compound like this. Similarly a third reaction also can be designed where the nitrogen is at the terminal position of the diene, it reacts with alkene to give you this heterocyclic compound.

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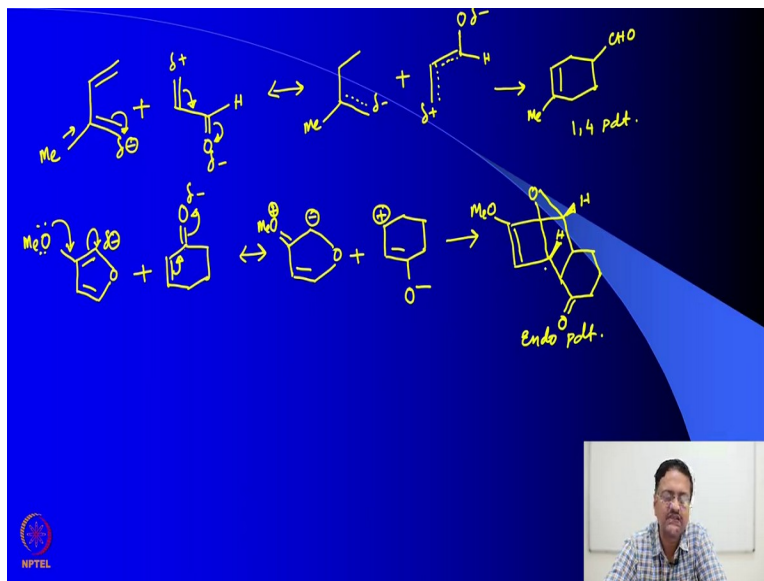


The other possible extension of this Diels Alder reaction is called the Imine Diels Alder reaction. So, in that case a C double bond N reacts with the diene and forms again a heterocyclic compound which I am trying to draw here. Of course we should maintain the stereo chemistry of Diels Alder adducts and we should remember that this is a regioselective reaction and this is also stereospecific reaction.

So, it gives you the trans isomer similarly if you have a diene which is a bit complicated diene that I am trying to draw this is a real example. So, this is a diene, dienophile and that contains the nitrogen as the source because as a C double bond N which is the imine bond. So, this particular reaction again takes place in this mechanism and what we end up getting is one heterocyclic compound that is a nitrogen and that nitrogen contains a CO_2Me group.

And it is trans to the corresponding phenyl and the double bond shifts here the Ph is here sorry the Ph is on the other carbon and this is the point where you have tertiary butyl group connected to the oxygen. So, this is the product that happens to be one of the examples of Imine Diels Alder reaction. So, with this we end our discussion on the Diels Alder reactions. So, before closing this discussion let us try to solve a couple of problems that I have already given to you in the beginning of this lecture.

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So, let us try to take the example number 4. So, this methyl group is electron donating. So, when it pushes electron the double bond here sort of tries to break and form a delta negative charge on that carbon. And this carbonyl group is electron withdrawing group. So, it pulls the electron and makes a delta negative here and delta positive at that end. So, what should happen is this charge separated resonating structure would have delta negative here plus delta positive there which if we try to draw opposite like that.

So, delta positive is here that double bond is forming this is the oxygen which is delta negative and hydrogen. So, as a result this would give you the product as the 1 4 product. Similarly let us try to see one example where we should think about whether it should be the endo product or the exo product and how the reaction should give you one compound out of two possible compounds.

So, this electron donating group pushes the electrons and it comes here and makes it delta negative this compound pulls electron outwards and then you get a delta negative charge there. So the charge separated resonating structure would look like this right. So, now when the reaction happens it gives you the Endo product if you try to remember then we should draw the product accordingly right.

So, this is how one should try to draw these products using the Diels Alder reaction. So, I would leave the other problems for you to work out one by one. And if you have any problem you can send email to the portal or directly send email to me then we will respond to your query, thank you. We will continue from here in the next lecture with some other addition reactions or rather condensation reactions, thank you.