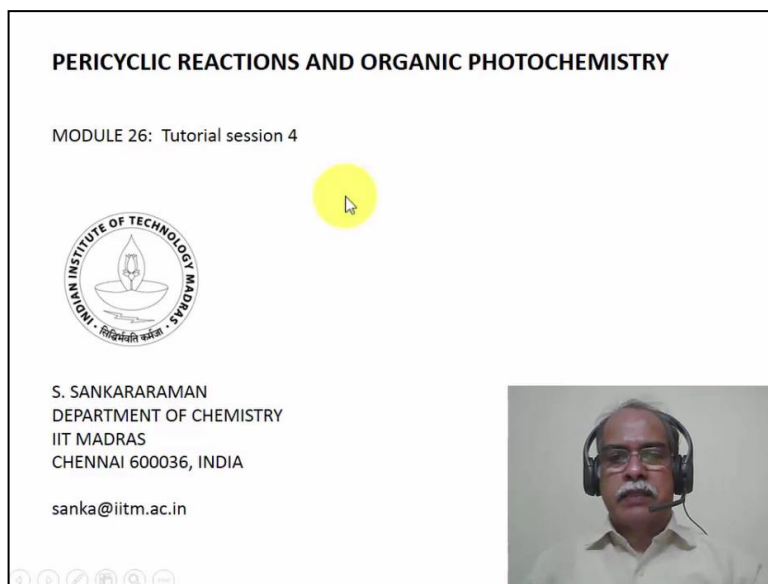


**Pericyclic Reactions and Organic Photochemistry**  
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**Module No. #06**  
**Lecture No. #26**  
**Tutorial Session 4**

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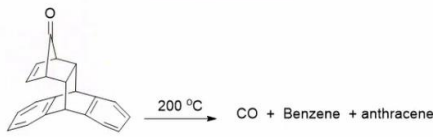
The screenshot shows a presentation slide with the following content:

- PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY**
- MODULE 26: Tutorial session 4
- The logo of the Indian Institute of Technology Madras, featuring a lamp and the motto "सिद्धयन्ति श्रद्धा" (Siddhanti Shraddha).
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- A small video inset in the bottom right corner shows the speaker, S. Sankararaman, wearing a headset.

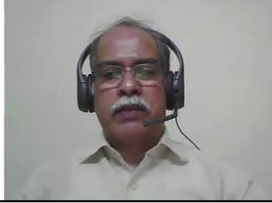
Hello, welcome to the online course on, Pericyclic Reactions and Organic Photochemistry. We are in the Sixth Week, in Module Twenty-Six, for example. And, this is a Tutorial session. This is Tutorial Session Number Four. In this tutorial, we will consider a variety of problems, pertaining to Pericyclic reactions, from Cycloaddition to Sigmatropic rearrangement, to Ene reaction, and so on. This is important, because this exercise will help you to identify certain problems, in the Pericyclic category.

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Two successive pericyclic reactions are involved in the following transformation. Identify the pericyclic steps.



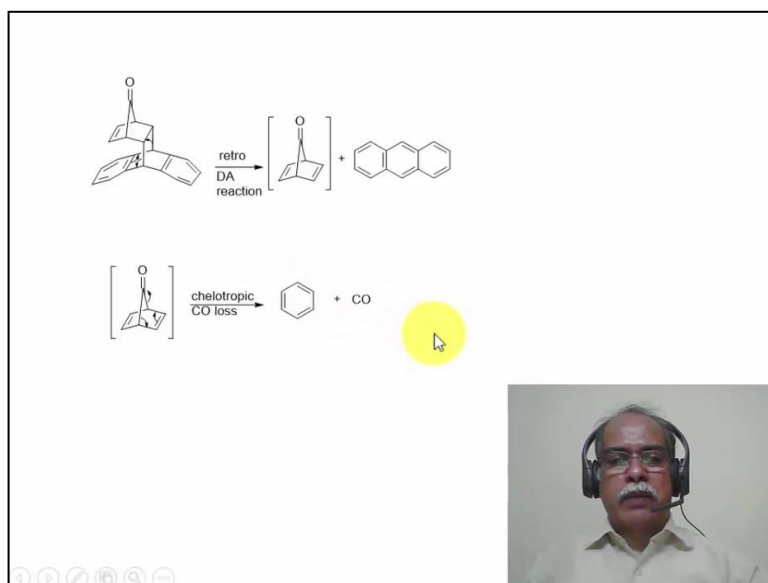
Anthracene undergoes Diels-Alder reaction as well as retro Diels-Alder reaction at the 9,10 positions. CO is formed probably by chelotropic elimination of a bicyclo[2,2,1]hepta-2,5-dien-7-one, which is formed in the retro Diels Alder step.



Now, the first problem is stated like this. Two successive Pericyclic reactions are involved, in the following transformation, identify the Pericyclic steps. In other words, this molecule is undergoing Thermal decomposition, to generate Carbon monoxide, Benzene, and Anthracene. Now, this particular molecule, if you look at, this is essentially a Diels-Alder addition product of this Bridged Ketone, which is a Dienone, undergoing a Diels-Alder reaction, with the Anthracene 9, 10 position.

In other words, Anthracene undergoes Diels-Alder reaction, as well as Retro-Diels-Alder reaction, at the 9 and 10 position. This is a 9th position, and this is a 10th position of Anthracene. Now, CO is probably formed, from a Chelotropic reaction of a, Bicyclo-Hepta-2,5-Dienone, which is a Dienone, which is coming from this particular moiety, which is formed in the Retro-Diels-Alder step.

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So, one can consider the reaction as initially, a Retro-Diels-Alder reaction, as indicated by these three small arrows, that are shown in this structure, which results in the formation of Anthracene, and this unstable [2,2,1]-Bicyclic Ketone. The [2,2,1]-Bicyclic Ketone, under the reaction condition, will not survive. It readily undergoes, the loss of Carbon monoxide, with the formation of Benzene, which is an Aromatic product.

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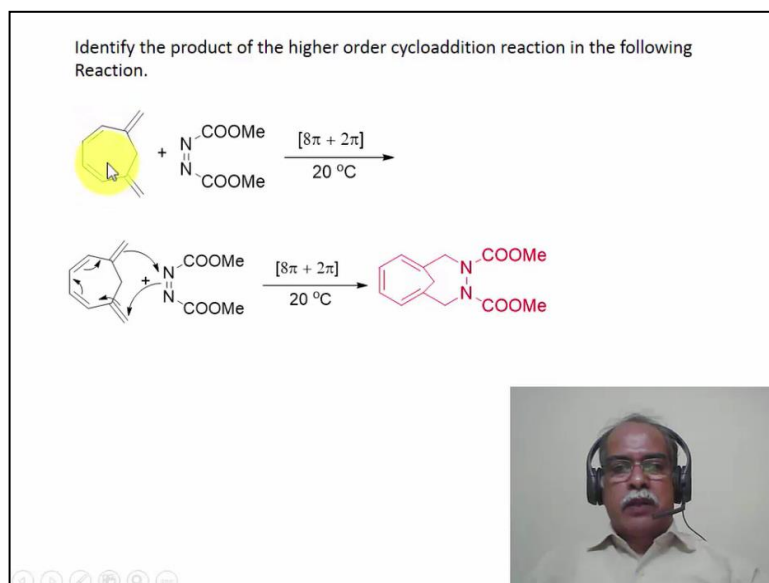
So, essentially this reaction, this particular molecule, undergoes initially a Retro-Diels-Alder reaction, followed by a Chelotropic elimination of Carbon monoxide, in the formation of Benzene and Anthracene, for example, in this reaction. It is a very interesting reaction.

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Because, the reactive intermediate like this one, is stabilized in the form of a Diels-Alder adduct, in this particular instance.

In fact, the forward reaction would be difficult to do, because this is not a readily available starting material. So, this molecule would have been prepared by a different route, other than a Diels-Alder reaction route, in this particular case.

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Now, the second problem deals with, again a Cycloaddition reaction of higher-order. Identify the product of the Higher-Order Cycloaddition reaction, in the following reaction. In other words, Dimethyl Acetal Dicarboxylate, which is acting as the Enophile, a Dienophile for example, and this is acting as a Polyene, which is undergoing a Higher-Order Cycloaddition reaction. The Higher-Order Cycloaddition reaction, is an 8PI-2PI-Cycloaddition reaction, as indicated on the arrow. It essentially takes place, at room temperature, around 20°celsius.

If you look at this molecule, this is Bis Exomethylene Cycloheptadiene. It can undergo a Cycloaddition process, across this Methylene, and this Methylene. In other words, this would be a cyclic 8PI system, which is undergoing the Cycloaddition reaction. This is the 2PI component, which is undergoing the Cycloaddition reaction.

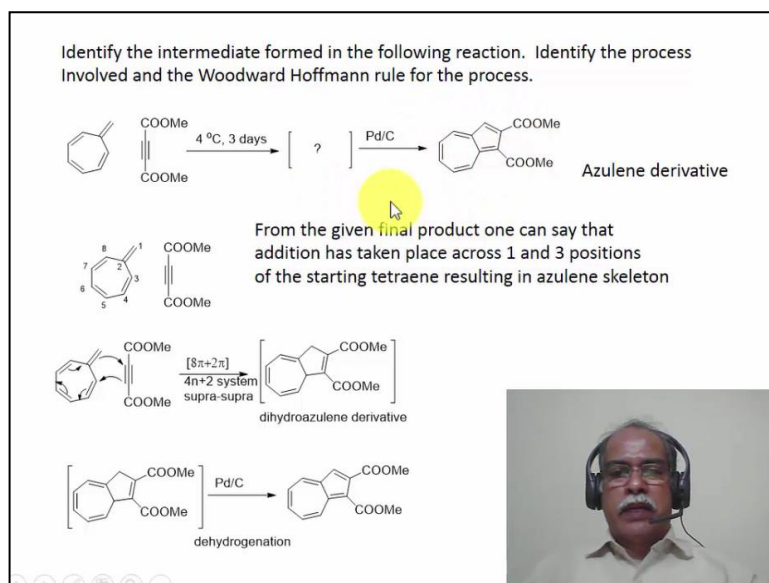
So, essentially the Cycloaddition product would arise, from the addition of this Carbon onto the Nitrogen, and this Nitrogen on to this Carbon, with the concomitant rearrangement of the PI system, in the cyclic system. So, that would result in the formation of this particular molecule. You can see here, the N-double bond-N, has become a single bond-N, because of the Cycloaddition process.

And, this two Methylene groups, are essentially appearing in this two positions, which are connected to the Nitrogen. And, this Methylene here, which is a SP<sup>3</sup> Methylene, is essentially acting as the bridge, in this particular system. So, this is a product of 8PI-2PI-Cycloaddition reaction. Since, the reaction is given in a straightforward manner, as an 8PI-2PI-Cycloaddition reaction, one can easily figure out the answer, for this particular question.

If this information is missing, it could be a misleading question. Because, one can think of a Diels-Alder reaction, and so on, with this molecule. This molecule has a Periselectivity. In

that, it undergoes only an 8PI-2PI-Cycloaddition reaction, not a 4PI-2PI Cycloaddition reaction, as it is also possible, in this particular case.

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Again, another example of a Higher-Order Cycloaddition reaction. Identify the intermediate formed, in the following reaction. Identify the process involved, and the Woodward-Hoffmann rule, for this particular process. What has happened is, an Exomethylene Cyclohexatriene, is undergoing a Cycloaddition reaction, with Dimethyl Acetylene Dicarboxylate, essentially at low temperatures, in the freezer. Although, it is a very slow reaction, it takes three days for this reaction to proceed, gives an intermediate.

The intermediate, on treatment with Palladium and Charcoal, has gone to an Aromatic compound, which is an Azulene derivative. This, 7-Membered-5-Membered fusion, is an Azulene ring. So, it is a Dimethyl Dicarboxylate ester of the Azulene derivative, is what is formed, in this particular case. So, one can think of a Cycloaddition process to take place, between Carbon Number 1 and 3, and Carbon Number 1 and 2 of the Acetylene. In other words, this Carbon, and this Carbon, can undergo Cycloaddition process.

Because, you need to form a 5-Membered ring fusion. So, this will be 1-2-3-4-5. So, 5-Membered ring can be formed, by this combination of 1-2-3, and this 4 and 5, coming from the Acetylene unit. So, the Cycloaddition process is mentioned here. That is essentially a, this is acting is an 8PI electron system, because of the rearrangement of the PI system completely, to give a Conjugated Triene unit, here. So, it is an 8PI-2PI-Cycloaddition reaction. It is a 4N+2 combination.

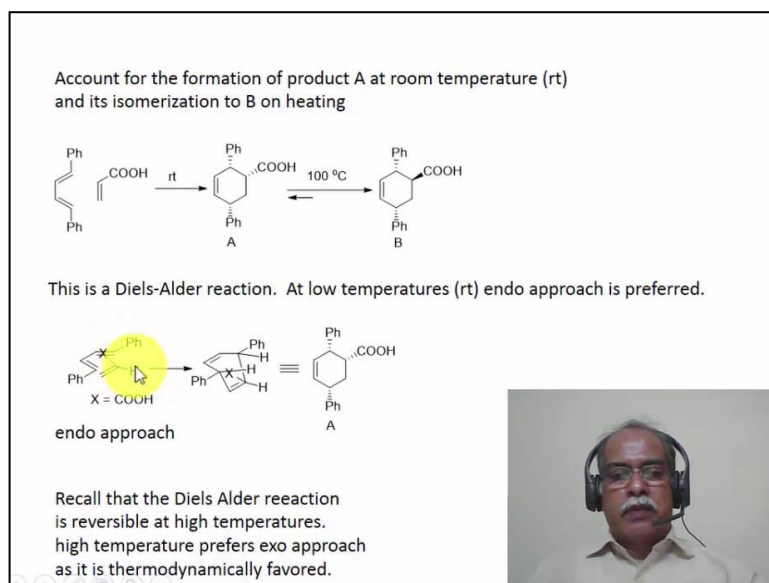
So, it is Suprafacial-Suprafacial, is allowed process, according to Woodward-Hoffmann rule. It is very similar to Diels-Alder reaction, which is also a 4N+2 Cycloaddition reaction. It is a

Suprafacial-Suprafacial Cycloaddition reaction. The product, that is formed, is not Aromatic. Because, this is not a fully conjugated. This is an Aromatic, because it is a 10-Annulene system. This is a 6+4, 10. And, it is Azulene, as a moiety. Azulene is a very well-known Aromatic compound. Whereas, this is a Dihydro Aromatic compound.

Because, this is an SP<sup>3</sup> Carbon here, and this is also an SP<sup>3</sup> Carbon. The Palladium and Charcoal is known to do Dehydrogenation, of Dihydro Aromatic compounds, to Aromatic compounds. So, the second step, that is involved in the process, is a Dehydrogenation process. The Dehydrogenation of the Dihydro Azulene, using Palladium and Charcoal, to give Azulene derivative, is the final step for this particular reaction. It is a very interesting reaction.

Because, this is one of the synthetic methodologies, to make Azulene derivatives, specifically substituted in this position. Or, if it is specifically substituted on this position also, one can think of alternatively, the substituted Exomethylene Cycloheptatriene as a starting material, to prepare Azulene as the molecule. So, one can take it as a Synthetic Methodology, to make Azulene derivatives of this type, by Higher-Order Cycloaddition reaction.

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Here is another interesting question. Account for the formation of Product-A, which is formed at room temperature, when this Diphenyl Butadiene, reacts with Acrylic acid. However, this on heating, A on heating, undergoes isomerization. You can see here, one of the center is a difference stereochemistry. This is All Cis stereochemistry. Whereas, this is [1,4]-Cis, and [1,2]-Trans kind of a stereochemistry. This is a Diastereo isomer, of this particular molecule.

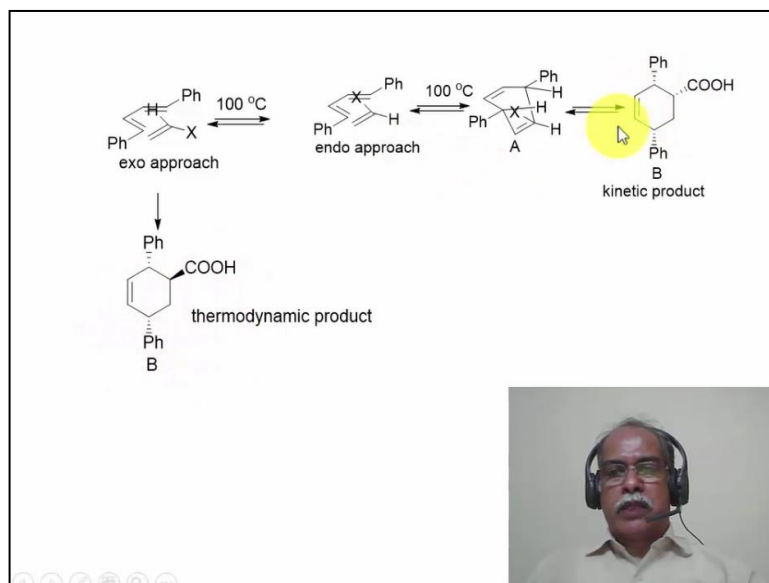
So, how is it formed. Initially, one can think of a Diels-Alder reaction, between these two molecules. As you know, Diels-Alder reaction is highly Endo selective, especially at low temperature. Because, this is a Kinetic product. The Endo product is Kinetic product, because of the Secondary Orbital interaction, that can take place. So, one can now think about a, Endo selective Diels-Alder reaction.

You can imagine, this Hydrogen in this position, containing the Phenyl group, and this Hydrogen in this position, and the Hydrogen in the Olefin, where X is a substituent COOH, they all point in the same direction, in the transition state. So, the product that is formed, would have the Phenyl groups, and the X-group, pointing in the same direction, backward. So, one can see the Phenyl COOH, and the other Phenyl, they are All Cis with respect to each other. And, this 3-Hydrogens are also, Cis with respect to each other.

This is the formation of A. In other words, this particular product, is same as this product, in terms of the relative stereochemistry of the 3-Centers, that are generated in this particular molecule. Now, how is it that, this is undergoing isomerization, to give this particular product, at high temperature. Now, please recall that, Diels-Alder reaction is a reversible reaction, at high temperature. In other words, the Retro-Diels-Alder reaction, can take place.

And, at high temperatures, in fact the Diels-Alder reaction, prefers Exo approach, which is a thermodynamically favored approach. The Endo approach, is kinetically favored, because the transition state is stabilized by, Secondary Orbital interaction. So, it has a lower activation barrier. Whereas, the Exo with the X functional group, pointing outward of the PI system, is thermodynamically more stable. Because, this is the least sterically hindered approach, of the Diene and the Dienophile.

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So, initially at room temperature for example, the Endo approach takes place, and the Endo product, is what is formed, in this case. This is a kinetic product. Sorry, there is a mistake here. This should be the kinetic product, that is formed, in this reaction. However, this reaction is a reversible reaction. At hundred degrees, of course, the initially formed adduct, can undergo Retro-Diels-Alder process, to give the starting material. This can now approach, in an Exo manner. The Endo approach, gives this product.

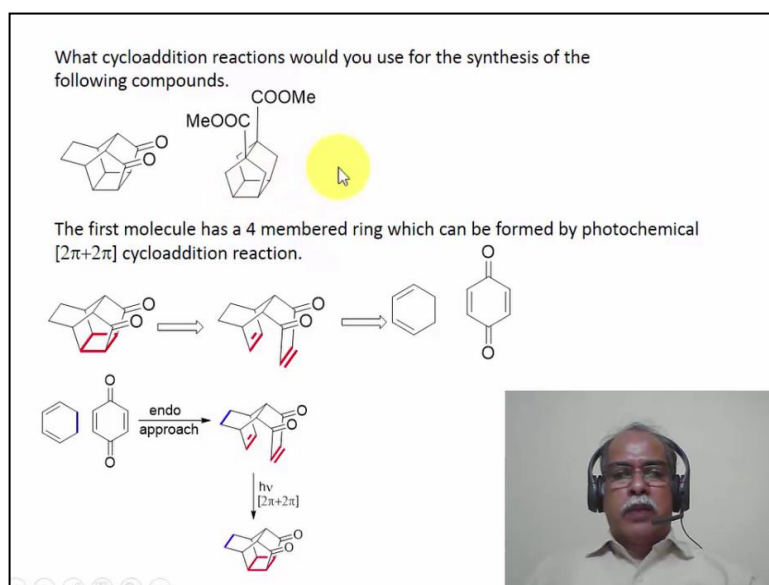
This should be, Product-A. This is not, Product-B. There is a mistake, that i want to point out. It should be A, here. Because, this is All Cis. This is also, All Cis. Now, the Exo approach would put the 2-Hydrogen outward, and this Hydrogen inward. So, the 2-Hydrogens in the [1,4]-positions, are Cis with respect to each other. Whereas, the Hydrogen containing the Carbon, bearing the COOH group, is Trans to this particular Hydrogen.

So, you can see here, this Hydrogen is pointing in the front, which is not shown, of course in the structure. This Hydrogen is pointing inward. Those 2-Hydrogen should be Trans, with respect to each other. So, this is the product, where you have [1,4]-Cis, and [1,2]-Trans, which is a thermodynamic product, in this particular case. So, this problem illustrates, two possibilities of Diels-Alder reaction.

The first possibility, is the Endo approach, at low temperature. And, of course at high temperatures, a Diels-Alder reaction can be reversible. Once it is reversible at high temperature, Diels-Alder reaction can be, Exo approach possibility. So, Exo approach gives a thermodynamically stable product, whereas the Endo approach gives the kinetic product. That is the message, you get from this particular problem.



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Here are, some interesting molecules, which needs to be synthesized by Cycloaddition reaction. The question is, what Cycloaddition reaction would you use, for the synthesis of the following compound. If you take this compound, this is a caged structure, and this is also a caged type of a structure. And, what is interesting feature in this molecule is a 4-Membered ring. As, we all know, the 4-Membered ring can be formed, by a 2+2 Cycloaddition reaction. So, i will give the example of this molecule, for the synthesis. You figure it out yourself, what is the starting material, for this particular molecule. I am not going to solve this problem. Because, once i solve this problem, an equivalent synthetic approach should be possible, for this molecule. The only clue, i can give here is, this Carbon, and this Carbon, bearing the 2-Esters, come from Acetylene Dicarboxylic acid. In another word, Dimethyl Acetylene Dicarboxylic acid is one of the reactants, for this particular molecule.

Take the clue, and do it yourself, to solve the synthesis of this, particular problem. I will deal with this problem. Let us, to start with, the first molecule has 4-Membered ring, which can be formed by a Photochemical-2PI-2PI Cycloaddition reaction. The 4-Membered ring is shown very clearly, in the Red color. And, the proposed 2+2 Cycloaddition reaction, is shown here. In other words, this molecule, when it undergoes a 2+2 Cycloaddition reaction, would give this molecule.

This is a Retro Synthetic arrow. We are doing a Retro Synthetic analysis, by putting the double bond here. In fact, the reverse reaction is what, one would perform to do the 2+2 Cycloaddition reaction. Now, this is a product, which is essentially a Diels-Alder product of Cyclohexadiene, [1,3]-Diene, and Benzoquinone, in an Endo approach. So, you can see here,

this Methylene bridge here, CH<sub>2</sub>-CH<sub>2</sub> bridge, is essentially coming from the, CH<sub>2</sub>-CH<sub>2</sub> of the Cyclohexadiene, undergoing a Diels-Alder reaction.

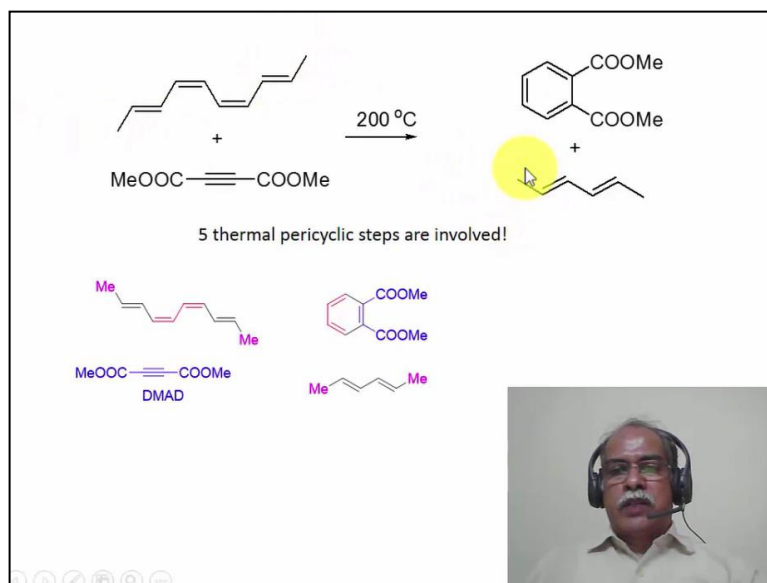
So, this 6-Carbon fragment, is essentially coming from the Dienone fragment, is coming from the Benzoquinone moiety, as the Dienophile. As you know, Benzoquinone is a powerful Dienophile. It will readily undergo, Diels-Alder reaction, with Hexadiene. So, the initial reaction is an Endo approach reaction. Essentially, this reaction can be performed, at room temperature. It does not need any heating, because of the high reactivity of the Benzoquinone, as the Dienophile. You can see here, this Methylene bridge, is shown in Blue color.

So, that is resulting in the structure, in the Blue color, that is shown here. And, the Olefin, that is formed here, and the Olefin, that is a residual Olefin, which does not react on to the Diels-Alder condition, or ending up in this close proximity, with respect to each other. Now, because of the Endo approach, and the close proximity, this is an Endo substituent, for this [2,2,2]-Bicyclic system, that would put this double bond, and this double bond, in close proximity. And, that is what, results in the 2PI-2PI Photochemical Cycloaddition reaction.

So, a Diels-Alder reaction between Hexadiene and Benzoquinone, would give you the precursor, which pushed the two double bonds, in close proximity in the Endo approach. And, this molecule is a precursor, for the final target molecule, which can be obtained by a Photochemical 2PI-2PI Cycloaddition reaction. So, this is a Thermal-4PI-2PI-Suprafacial-Suprafacial Cycloaddition. This is a Photochemical-2PI-2PI, which is also a Suprafacial-Suprafacial Cycloaddition process.

So, the two Cycloaddition process, would result in the synthesis, of this compound. You can also imagine, the same kind of a strategy for this. Already, clue is given. The Dimethyl Acetylene Dicarboxylic acid is one unit. And, imagine that, this 4-Membered ring is going to be formed, by a 2PI-2PI Cycloaddition process, of a suitably substituted precursor, or synthesizing this molecule. So, solve this problem yourself, so that it gives you, some exercise to do, in terms of identifying the process involved, and the starting materials involved, in the synthesis.

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Now, here is a question. When, this Tetraene, and the Dimethyl Acetylene Dicarboxylic acid, are heated together, at 200°celsius, the product formed are, Dimethyl Phthalate, and Butadiene, which is Dimethyl Substituted Butadiene. There are five Pericyclic steps involved. This is a clue, that is given in this, solving this problem. So, one has to find out, what kind of a connectivity exist, in the final product, which arises from the fragments, of this particular molecule.

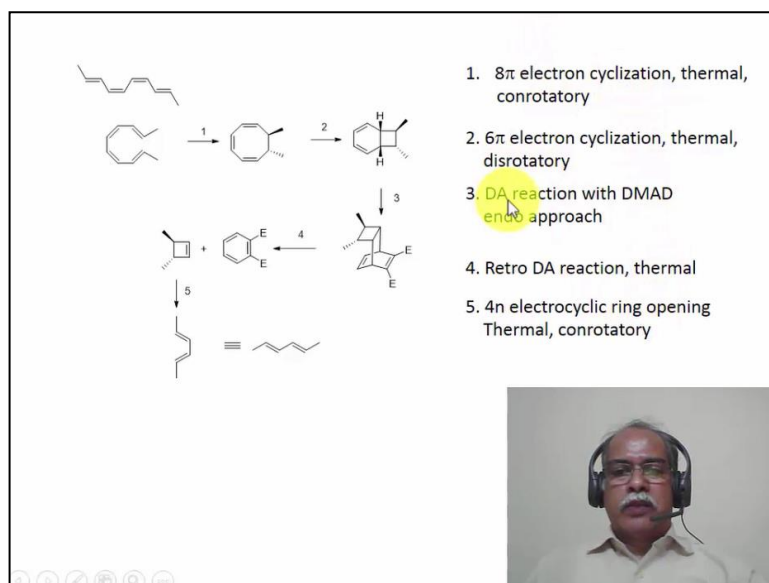
You can clearly tell that, this Diester, and these two Carbons, the Ortho Carbons, and the Diester, should come from, the Dimethyl Acetylene Dicarboxylic acid. So, i have written the Dimethyl Acetylene Dicarboxylic acid, in Blue. And, this Blue fragment in the product, which is this particular product, should essentially come from the Dimethyl Acetylene Dicarboxylate. Now, the Red portion, which is the Diene portion, in this molecule, essentially should come from the Diene, of this particular molecule.

So, the Red portion here, should correspond to the Red portion, here. And, this Black portion, which is the Diene portion, essentially should come from this Olefin, and this Olefin. Somehow, the connectivity should be made here, between them. Finally, the two Methyl groups, essentially come from the two Methyl groups, which are in the starting material. So, which is, there are two or three things, which you can say unambiguously.

The Methyl groups are present, in the primal Product, as well as in the starting material. So, this Methyl, and this Methyl, should come from, essentially these two position, should result in the formation of this. And, the 2-Ester group, and this connecting Carbon, should also come from the Dimethyl Acetylene Dicarboxylic acid. That much, one can say for sure, in

this molecule. Now, when you take a Tetraene like this, it has a propensity to undergo, the Electrocyclic ring closure reaction.

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This is written, in the Transoid conformation. If you write it in the Cisoid conformation, which is this molecule. These two are equivalent molecule, identical molecule. You can see here, there is a Trans double bond, Cis double bond, Cis double bond, and a Trans double bond. So, you start from Trans, Cis, Cis, and Trans. This is the same molecule, as the one, that is shown here. The reason, it is written in the cisoid conformation is, so that, you can do the Electrocyclic ring closing process, across Carbon Number 1, and Carbon Number 8, of this Octatetraene.

So, the Octatetraene, undergoes the Electrocyclic ring closing reaction, which is a thermal reaction, at  $220^{\circ}$  Celsius. And, it should a  $4N$  electron system. It is an 8-Electron system. And, it should be a Conrotatory process. The Conrotatory ring closure occurs. Carbon Number 1 and 8, will essentially put these two Methyl groups, Trans with respect to each other. So, one gets a Trans Dimethyl substituted Cyclooctatriene molecule. And, this does not still put like this. It further undergoes, Electrocyclic reaction.

This is something, we have seen, during the course of the Electrocyclic reaction, that we studied in the earlier modules. So, this is behaving like a 6-Electron system. 6-Electron Thermal cyclisation is a Disrotatory cyclisation. So, the Hydrogen in this position, and the Hydrogen in this position, end up Cis with respect to each other, informing this [4,2,0]-Bicyclic system of this kind. So, we have now done, two Pericyclic steps. One is an 8-Electron cyclisation, which is a Thermal Conrotatory process.

The other one is a 6-Electron cyclisation, which is a Thermal Disrotatory process, resulting in the formation of this molecule. Now, this molecule can undergo Diels-Alder reaction, with the Dimethyl Acetylene Dicarboxylate. So, essentially that is a process, that is going to take place. This is an Endo selective, Dimethyl Acetylene Dicarboxylate up Endo approach, to produce this particular molecule. In other words, compared to these 2-Hydrogens, which are pointing in this direction.

The Dimethyl Acetylene Dicarboxylate, should come from the side of this 2-Hydrogen, rather from the side opposite of this 2-Hydrogen, which will be hindered by this bridge, for example. So, the least hindered approach, is the Endo approach, in this particular case, resulting in the formation of this particular product. This is a 4PI-2PI Cycloaddition reaction. So, it is a Suprafacial-Suprafacial Cycloaddition reaction, is what is taking place. Now, this is a strained molecule.

This can undergo, Retro-Diels-Alder reaction. Essentially, one of the molecule is already produced. This is a Dimethyl Phthalate, is what is formed here. Phthalic acid ester, Dimethyl ester of Phthalic acid is produced here.

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That is one of the product, here. If you can see here, this is one of the product. So, we have already formed, that particular product, here.

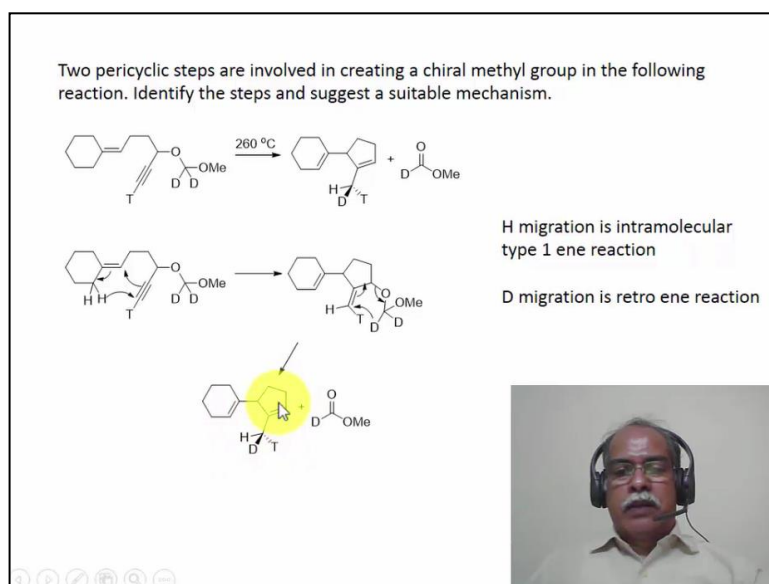
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And, this is a Retro-Diels-Alder reaction, which is forming the Cyclobutene derivative.

In other words, Trans Dimethyl Cyclobutene derivative is formed. Under the reaction condition, it will open up, in a Conrotatory fashion. It is the Retro Electrocyclic ring opening reaction, under thermal condition, to produce this. This is essentially, same as this molecule. So, these are the two final products, that are indicated in the earlier slide. So, the 5-Pericyclic steps, are also identified, very clearly here.

The first one is 8-Electron cyclisation, then followed by a 6-Electron cyclisation. A Diels-Alder reaction, followed by a Retro-Diels-Alder reaction. Finally, a 4N cyclisation, is what is done. So, when you take this molecule, Dimethyl Acetylene Dicarboxylate, and heat it strongly to 200° or so, for a prolonged period of time, these are the two thermodynamically stable products. This is an Aromatic Product, and this is of course, a Conjugated Diene product.

These are the two products, that are formed. Perhaps, the driving force is the formation of this Aromatic product, coming from the Retro-Diels-Alder reaction, which drives the overall reaction, to the formation of this two products, that are formed, in this reaction. A very interesting molecule, because, it is a very challenging problem, to identify each step, with the Pericyclic selection rule, and so on. So, i thought, i should present this to you, in this manner. (Refer Slide Time: 20:55)



Another interesting problem. You are generating a Methyl group, which is a Chiral Methyl group. Here is 1-Hydrogen, 1-Deuterium, and 1-Tritium, substituted on the Methyl group. So, that makes this Methyl group, a Chiral Methyl group. There are two Pericyclic reactions, involved in creating the Chiral Methyl group, in the following molecule. Identify the steps, and suggest a suitable mechanism, for this reaction. If you look at the starting material, there are Hydrogens in these positions, which are Allylic Hydrogens

There are Deuterium, in this position, which are sort of, Acetal kind of a linkage, is what is given here, to form. So, the Hydrogen from this position, can be transferred onto this one, to get this Hydrogen. In the process, you will do a [1,5] kind of a shift, is what, you are doing. In other words, you can think of a Ene reaction, which is a [3,4] Type-1 Ene reaction, is what we are, going to perform here.

so, take this Allylic Hydrogen, push it over here, with the concomitant rearrangement of the Diene units here, to form the connectivity between this Carbon, and this Carbon, will essentially produce the 5-Membered ring. So, the first reaction essentially, is to identify the Ene component. the Ene component is identified very clearly, as a [3,4] Type-1 Ene reaction. so, this is the Ene component, and this is the Enophile component. the Acetylene is a Enophile component, which is already Tritium substituted.

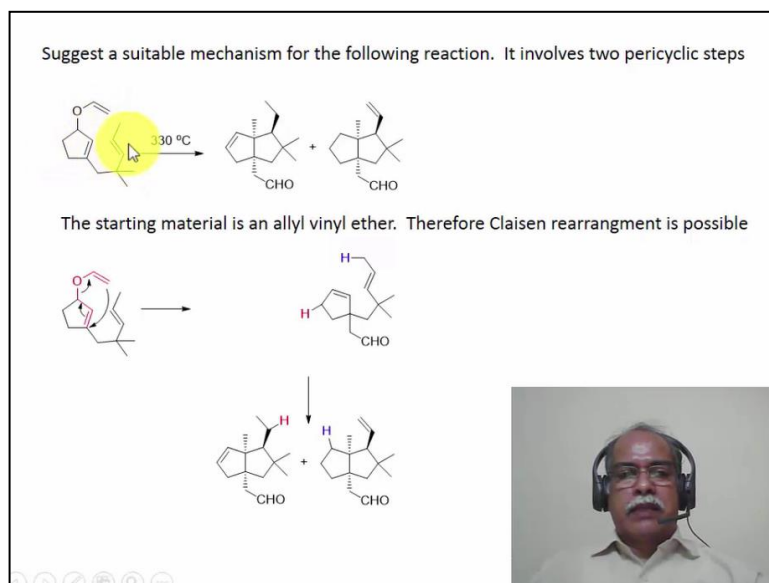
So, the Ene reaction is shown here. the Hydrogen is shifted over here, with the concomitant formation of the Carbon-Carbon bond, and the re-organization of the PI bond onto the system, resulting in the formation of the Hydrogen Deuterium substituted derivative, which is this particular derivative. now, all you need to do is, shift this Deuterium, over here. this should be a Suprafacial process. Remember, this is a [1,5]-Hydrogen shift. So, it is a Suprafacial-Suprafacial process, is what is going to take place.

Here is a Deuterium, transfer onto this position. If you consider this, actually this is a Retro Ene reaction, is what this product is. Retro Ene reaction, is what you need to perform, in order to do this Deuterium transfer, over here. I will show that, very clearly. You can transfer the Deuterium over here, with the loss of the Deuterated Methyl formate, as the molecule. In other words, if you do a Ene reaction, between this two, you will get this molecule.

The Deuterium transfer over here, on to this Carbon, with the concomitant formation of a Carbon Oxygen bond, should give this. So, the reverse reaction is a Ene reaction. The forward reaction, as it is shown, is the Retro Ene reaction, is what is performed. So, transfer of the Deuterium, on to the Methylene, which has the Hydrogen and Tritium already, produces the Chiral Methyl group. It is not an Enantioselective synthesis. It is an interesting way of making a Chiral Methyl group, in a Racemic form, in this particular case.

The Hydrogen migration is Intramolecular Type-1 Ene reaction. The Deuterium migration is a Retro Ene reaction. I hope, you have got the Retro Ene properly, in this particular instance. This is a Retro forward direction. In the reverse direction, you can imagine, this to be an Ene reaction, between Deuterated Methyl formate, and this particular Ene component, which is having an Allylic Deuterium, in this position, like this.

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Finally, we come to this problem, which is a mechanistic problem. Suggest a suitable mechanism, for the following reaction. It involves two Pericyclic steps. You can see here, there is a formation of a 5-Membered ring, between this position, and this position. Or, you can imagine, there is a cyclisation process, that has taking place, to give this two products. Now, if you take this molecule, what is that, one can readily identify. One can readily identify, the Allyl Vinyl Ether portion, very clearly.

So, one can see here, the Red portion correspond to the Allyl Vinyl Ether. Allyl Vinyl Ether, under thermal conditions, would undergo Thermal Claisen rearrangement. So, therefore, Claisen rearrangement is a possible reaction, for this molecule. The arrow shows, very clearly the mechanism, for the thermally induced Claisen rearrangement, that puts the CH<sub>2</sub>, CHO group, in this position, resulting in the formation of this particular molecule.

Now, this is the same molecule, i am flashing a name. This molecule has the necessary structural features, that can undergo the Ene reaction. In the Ene reaction, the Enophile can be this Allylic Hydrogen. So, this could be the Ene component, and this could be the Enophile component. Alternatively, this could be the Ene Component, and this could be the Enophile component. Essentially, you have to form a bond, between this Carbon, and this Carbon, to make this Fused Bicyclic Pentene system, of this kind.

Two 5-Membered rings being fused in a Cis fashion, with respect to these two positions. This Hydrogen, and this CH<sub>2</sub>O, CHO groups, are Cis with respect to each other. So, if the Ene reaction is taking place, by the Blue Hydrogen, migrating onto this position, with the formation of this one. Then, that would form essentially, this particular product. The Hydrogen is migrated to this position, the Blue Hydrogen. So, this product would correspond to the Ene reaction product, arising from this as Ene, and this as a Enophile.



If you take the Red Hydrogen, and migrate it to this position, that would correspond to the other Product. Again, formation of the Carbon-Carbon bond, between these two Carbon, is necessary for that Ene reaction, also. So, two simultaneous Ene reactions, from different positions as Ene component, and the Enophile component, essentially produces these two products. The Cis stereochemistry is essentially dictated, by the Suprafacial-Suprafacial migration of the Hydrogen, onto this position, resulting in the formation of the Carbon-Carbon bond, here.

So, that makes these two position, Cis configuration. And, this substituent is Trans, with respect to this. So, essentially one can explain, using a transition state structure, involving a 5-Membered cyclic transition state, in a Suprafacial-Suprafacial manner, to produce this two component, in the stereoselective manner, that it is shown, in this particular transformation.

Very interesting way of 5-Membered fused bicyclic systems of this type, using a simple open chain structure like this, by a Claisen rearrangement, followed by couple of Ene reaction. I hope, a variety of problems, that are discussed in this particular module, will help you think carefully about the, way to solve the Pericyclic reaction problem. I hope the examples, that are given, are interesting to you. Thank you very much, for your kind attention.