Transcriber's Name Angela

Pericyclic Reactions and Organic Photochemistry

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Module No. #02
Lecture No. #06

Introduction – Pericyclic Reactions – Electrocyclic Reactions – Tutorial Session 1

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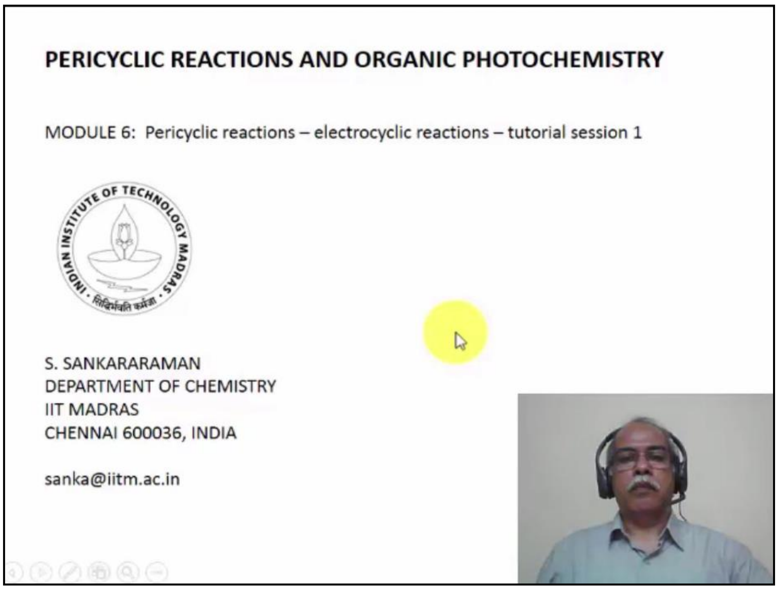

PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

MODULE 6: Pericyclic reactions – electrocyclic reactions – tutorial session 1

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Hello, welcome to the course on Pericyclic reactions and Organic photochemistry. We are into the second week of the course, starting with module six of the course. In module six, i thought, we will do the tutorial session, trying to solve some problems. By solving the problems, you become more and more familiar with the concepts, the Woodward-Hoffmann rules, and so, on, as far as the Pericyclic reactions are concerned. Moreover, the problems can be asked, in so, many different ways of the same reaction. I will illustrate it with couple of examples, in the subsequent slides here.

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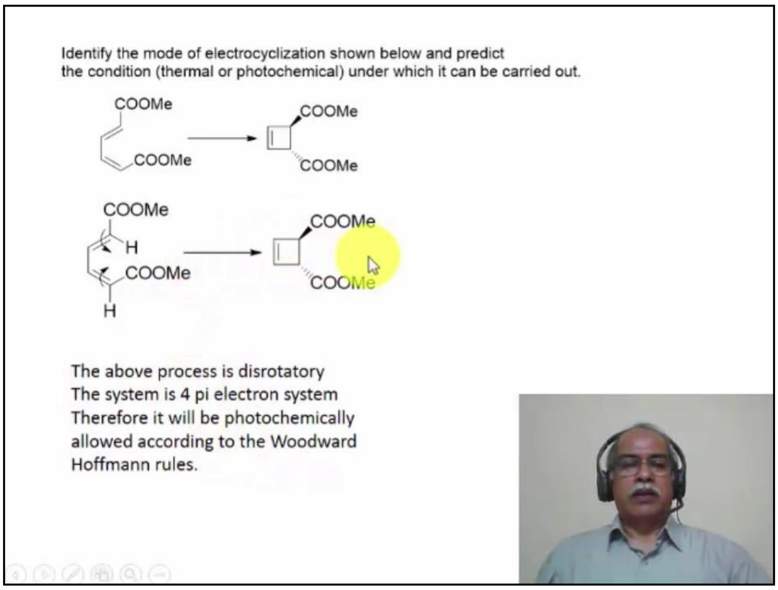

Identify the mode of electrocyclization shown below and predict
the condition (thermal or photochemical) under which it can be carried out.

The above process is disrotatory
The system is 4 pi electron system
Therefore it will be photochemically
allowed according to the Woodward
Hoffmann rules.

Let us start with this particular problem. The problem says, identify the mode of electrocyclization shown below, and predict the condition, whether it is a thermal condition or photochemical condition, under which the reaction can be carried out. So, this is a simple electrocyclic reaction. The starting material structure is given. And, the product structure is also given.

All you have to do is, figure out, what is the kind of cyclization, that would have taken place for this isomer, to produce this particular isomer, namely the Z E Isomer of the diene, to produce the Trans Isomer of the diester, Cyclobutene product, that is shown on the right-hand side. Now, in order to convert this molecule into this, you need to first count the number of electrons, that are involved.

This is a four-electron system. And, for a four-electron system, we can have either, a conrotatory process or a disrotatory process. In fact, in order to get this Trans isomer, you have to do only a disrotatory process. Then only, you will get the, one of the ester groups up, the other ester group down. And, this is illustrated in the answer, that is given here. So, if you do a disrotatory process, as it is shown by the arrow, stressing these bonds in this particular manner, this ester group will go down, and the Hydrogen will come up.

So, the ester is gone down, and the Hydrogen is up, which is not shown in the picture, in the structure. In this particular case, the ester group will come up, and the Hydrogen will come down. So, the ester group is up, and the Hydrogen is coming down, in this particular structure. So, essentially the disrotatory process of a four-electron system, is what has taken place. And, that alone will yield, this particular Stereo Isomer of the product, starting from this particular Stereo Isomer of the starting material.

Therefore, the conclusion is, the above process is a disrotatory process. Because, disrotatory process alone will account for the Stereochemistry of the product. This is a four Pi electron system. So therefore, the disrotatory process will take place, only under photo chemical condition. Because, only under the photochemical condition, this is a Woodward-Hoffmann allowed process. So, that is the answer. The precise answer is given in words, here.

And, the reaction mechanism is depicted in the scheme here, which constitutes the complete answer for this particular problem. The same problem could have been asked, by giving the condition, and asking you to write the structure of the product. That is one possibility. Or, both the structure and product would be given, as it is given here, for example. You will be asked to predict the reaction condition, and the mode of the reaction, just like the way the question is framed here, for example.

Alternatively, the conditions can be given, the mode of cyclization can be given, the product structure could have been given, and asking for the suitable starting material, that would yield this. So, this question can be framed in, so many different ways. Essentially, if you understand the concept, as well as understand the Woodward-Hoffmann rule, you will be in a position to answer this, without worrying about, what is the format of the particular question.

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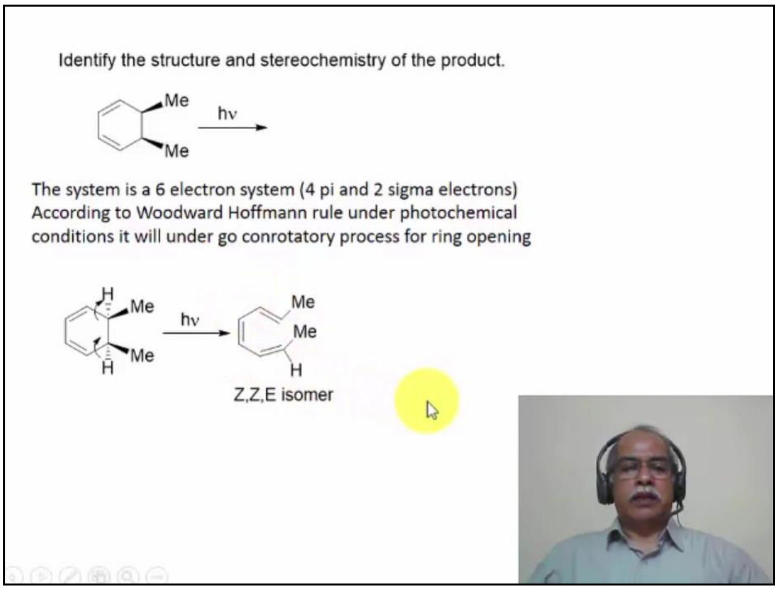

Identify the structure and stereochemistry of the product.

The system is a 6 electron system (4 pi and 2 sigma electrons)
According to Woodward Hoffmann rule under photochemical
conditions it will under go conrotatory process for ring opening

Z,Z,E isomer

It is another question. Identify, the structure and Stereochemistry of the product. It seems like a straightforward question. The structure of the starting material is given. The condition is given as a photochemical condition. This is a six-electron electro cyclic ring opening reaction. A six electron electrocyclic ring opening reaction, under photochemical condition, will happen only under the conrotatory mode. So, the six-electron system, why is this a six-electron system. The two Sigma electrons are involved, and the four Pi electrons are also involved, in the electro cyclization. That is why, it is a six-electron system.

And, according to the Woodward-Hoffmann rule, under photochemical condition, it will undergo only a conrotatory process, which is an allowed process. So, the answer is, the conrotatory process essentially will take care of the Stereochemical aspect of the product, that is being generated. In the sense that, the Hydrogen will come out, and the methyl will go in, of this particular carbon.

And, in this particular carbon, the methyl will go out, and the Hydrogen will come in. So, the Stereochemistry of this particular product, that is formed, the Hexatriene that is formed, is the Z Isomer of this particular double bond. This is already an Z isomer. And, this is a E isomer. So, Z Z E Isomer of the Hexatriene is what is being formed, as the only product in this particular reaction.

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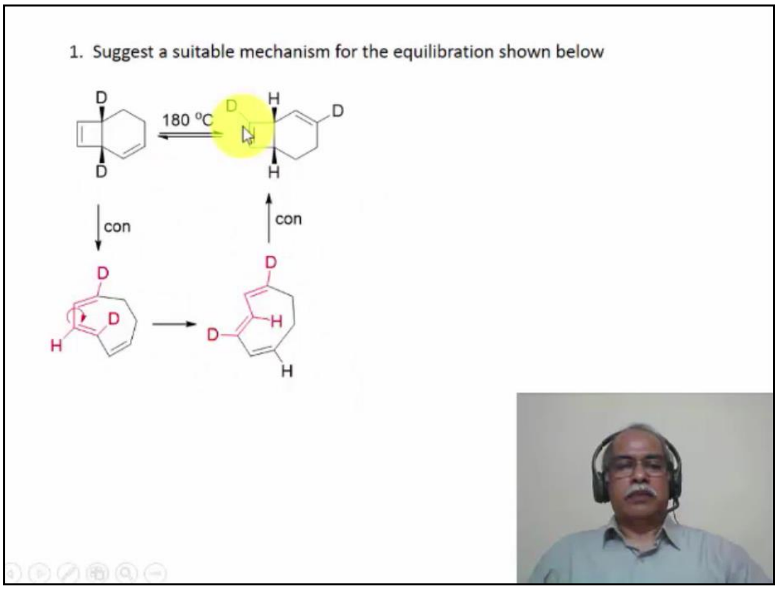

1. Suggest a suitable mechanism for the equilibration shown below

Now, this question, ask you to suggest, a suitable mechanism for the equilibration, that is taking place. Now, if you look at the structure carefully, the Deuterium atoms, that are present in the system, is separated by four carbons. You start counting from here. Carbon number one, carbon number two, carbon number three, and carbon number four. If you follow the cursor moment, you will see that, it is separated by four carbons. In the product also, it is separated by four carbons. Carbon number 1,2,3, and 4.

So, some molecular rearrangement, must have taken place. And, looking at the structure of the starting material, it is a Cyclobutene derivative. The product is also a Cyclobutene derivative, except the Deuterium's are dispersed in a different manner. So, at 180 degrees, the most likely reaction, that is going to take place for this particular molecule is, the opening of the Cyclobutene as the ring opening reaction. So, the Cyclobutene actually undergoes a ring opening reaction, by a conrotatory process. Because, this is a Cis fused system.

The conrotatory process will put, one of the Deuterium inside, and the other Deuterium outside. So, essentially you will get an eight-membered ring, with a Trans double bond, in this particular case. Now, this has to undergo a reorganization of the Pi system, such that, this Pi bond, which is the red Pi bond. In other words, the Cyclobutene carbons are now shown in the red, for example.

The Deuterium's are also shown in the red color, indicating, that the ring opening has taken place, in a conrotatory fashion, to give this. You can do the conrotatory process, in the other way around also, and push this Deuterium inside, and this Hydrogen also outside. That is also one possibility. But, that will not lead to the product, that is given here. That will be not be possible, to cyclize it for that, to get this particular product.

So, one of the ring opening process, that is taking place is the ring opening, as it is shown in this particular picture, to give the Deuterium inside, and other Deuterium outside. Now, if you rotate this carbon-carbon single bond, this is just a conformational change in this molecule. The Trans double bond, remains as Trans double bond, except the single bond is rotated, to bring the Deuterium out, and the Hydrogen in, such that, you make a Cisoid diene, out of this particular molecule.

Now, the Cisoid diene will undergo, the electrocyclic ring closing reaction, in the conrotatory fashion, to give the two Hydrogen, this Hydrogen, and this Hydrogen. One is inside. The other one is outside. It is exactly the reverse process of, what has happened here is, happening here.

This molecule, undergoes electrocyclic ring closing reaction, to give the Cis fused configuration, because of the two Hydrogen. Being conrotatory mode, it will undergo rotation, such that, the two Hydrogens will either come up or come down. In other words, they will be Cis with relative to each other. So, the product is formed. So, the mechanism is electrocyclic ring opening reaction, followed by a slight conformational change, followed by an electrocyclic ring closing reaction, to give this product.

So, this has to be worked out in detail, by understanding the point that, this is a 4N electron system, a strained system, which will undergo the electrocyclic ring opening reaction. The electrocyclic ring opening, these are energetically, there is no difference between, these two molecules. So, they can be in equilibrium with respect to each other. So, this proceeds essentially through a ring opening reaction, followed by a ring closing mechanism. That is shown here, in this Transparency.

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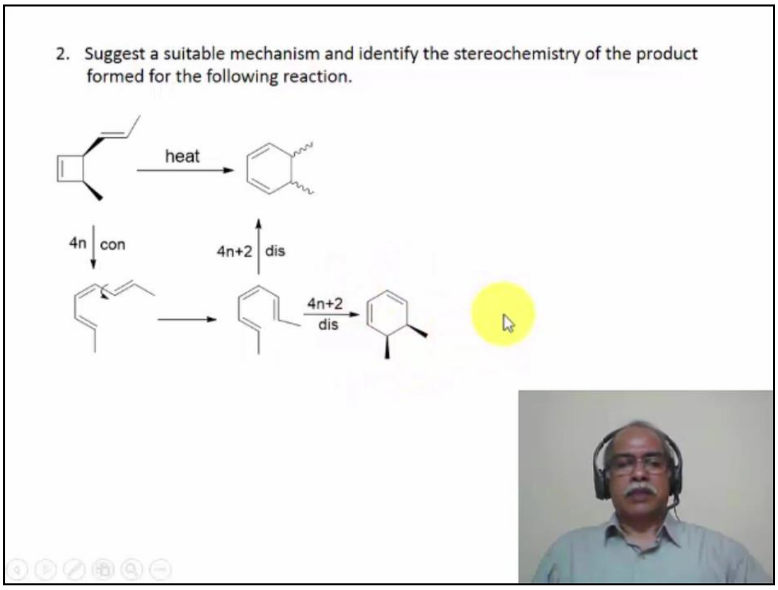

2. Suggest a suitable mechanism and identify the stereochemistry of the product formed for the following reaction.

Now again, another reaction, to suggest a suitable mechanism, and identify the Stereochemistry of the product, formed in the following reaction. Here, what is in is, you have a. In this particular case, you have a vinyl pentane group, which is part of a cyclic system. This problem is not very different. There is a vinyl pentane group, which is not part of a cyclic system. It is an acyclic vinyl pentane group, is what is given here.

So, much easier problem, compared to the earlier problem. Upon heating, the Cyclobutene will undergo ring opening reaction. The ring opening reaction product is given here, by conrotatory process. One of the methyl group will come out, the other methyl group will go in, during the conrotatory process. Because, this is a Cis directive, that we are talking about.

Now if you rotate this carbon-carbon bond, you can bring all the six Pi electrons in a Cisoid manner, which will now readily undergo, a six Pi electron cyclization. The six Pi electron cyclization is a disrotatory process, under thermal condition. So, the disrotatory process essentially will bring both the methyl groups, either up, or simultaneously up, or simultaneously down, does not matter, how it is written.

The relative Stereochemistry of the two-methyl group is CIS, with respect to each other. So, the product is given, only the Stereochemistry has to be identified. And, the mechanism is essentially a ring opening, followed by a ring closing of a different kind, in this particular case. In the earlier example, it is the four-electron ring opening, and the conformational change, again four electron ring closing, is what is taking place.

In this example, a four-electron ring opening reaction. And then, the sixth electron, five and six electrons, come from the vinyl group. It becomes a six-electron system, which undergoes the ring closing reaction, to give Cyclohexadiene, as the product. So, this is a product with Cis Dimethyl Stereochemistry, as the product structure.

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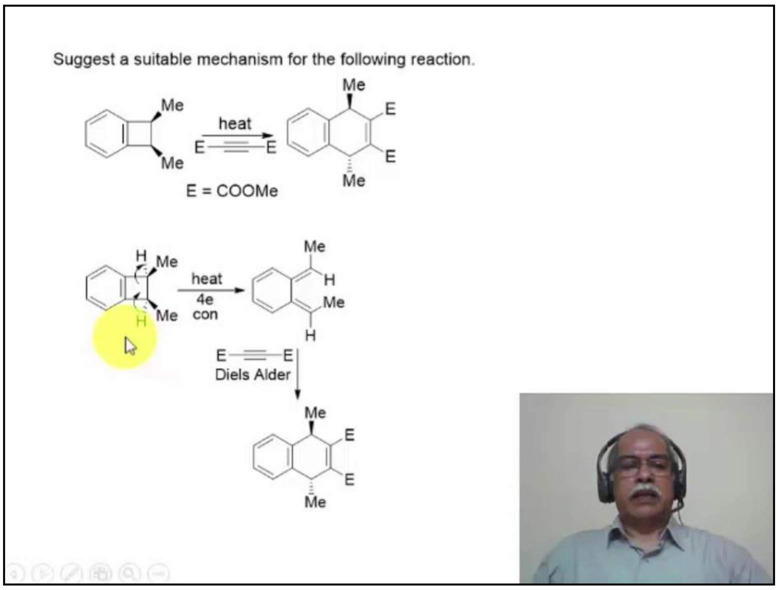

Suggest a suitable mechanism for the following reaction.

Now, again i suggest a suitable mechanism for the following reaction. The reaction is given. This is a Benzcyclobutene derivative. Something has happened to the Benzcyclobutene derivative on heating, in the presence of dimethyl acetylene dicarboxylate. The two e-groups are ester groups. So, this is essentially dimethyl acetylene dicarboxylate, as the product. What has happened is, there was two carbons have been added to the structure.

The two-carbons are essentially coming from, the dimethyl acetylene dicarboxylic acid. The acetylene carbons are coming here. You can identify, this unit being present, in this particular system. So, somehow, a Cycloaddition reaction has taken place, for the product to be formed, under this condition. The most likely mechanism is that, the Cyclobutene, which is a Benzcyclobutene in this particular case, will undergo thermal electrocyclic ring opening reaction, to give a diene.

So, the diene structure is shown here, by a conrotatory process. Once again, the two methyl groups are CIS, with respect to each other. So, one of the methyl will come inside, the other methyl will go out of the Pi system, upon the conrotatory electrocyclic ring opening reaction. Now, this is a diene, which can readily undergo Diels-Alder reaction. Because, that in the process of doing the Diels-Alder reaction, this ring gets its aromaticity, back.

So, the Diels-Alder reaction takes place, by the trapping agent, namely dimethyl acetylene dicarboxylic acid. And, these two methyl groups are Trans, with respect to each other. This is a 4 PI, 2 Pi electrons, Diels-Alder reaction is Cycloaddition reaction, is what is taking place. The Stereochemistry at the carbon number one, and carbon number four, can be easily explained, based on the fact, that is a suprafacial-suprafacial reaction, overlapping reaction. So, the methyl group that is inside, and this methyl group in this outside of the Pi framework, will end up, with respect to each other Trans Stereochemistry.

So, the one four Stereochemistry, essentially arises from the Stereochemistry of the diene itself, which is this particular diene, that we are talking about. I hope this is clear. So, fairly simple reaction of electrocyclic ring opening, followed by a Diels-Alder reaction, that would explain the formation of this particular product.

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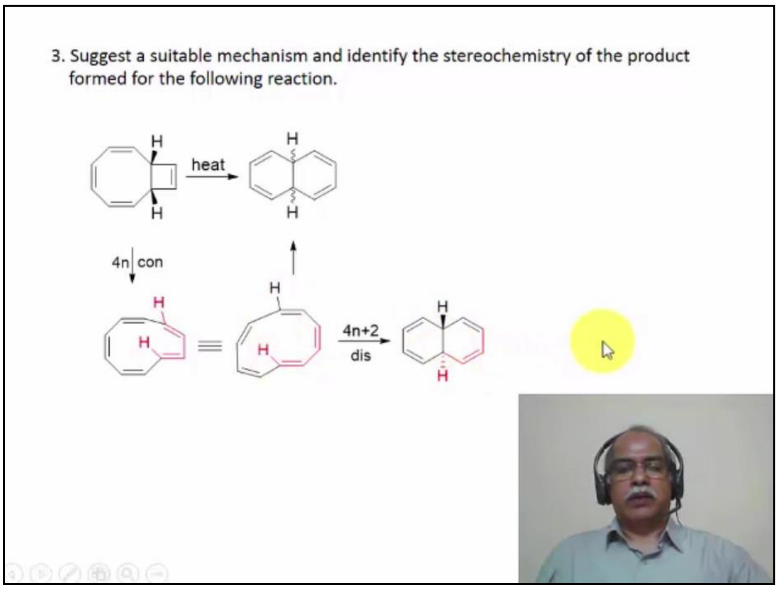

3. Suggest a suitable mechanism and identify the stereochemistry of the product formed for the following reaction.

Again, suggest a suitable mechanism, and identify the Stereochemistry of the product. This seems to be, a slightly a larger ring system. Does not matter, how large it is. As long as, you can keep track of the number of electrons, that are involved in the reaction, then that should suffice. Now, this is again a Cyclobutene derivative. So, on heating, most likely, it will release its strain and become a larger ring system. Let us see, what happens, when you heat it. A conrotatory process is what, is going to take place.

One of the Hydrogen will come inside, the other Hydrogen will go out. So, we have this particular Stereochemistry of the product. Now, if you look at the structure of the starting material and the product, the number of carbons are exactly the same, except this is a fusion, is different. This is an eight-membered ring, fused to a four-member ring. 8 +2 is 10. Whereas, this is a six-membered ring, fused to another six-membered ring. Two, six-member rings are fused together.

So, this is 6+4 10. The number of carbons are essentially remains the same, in this particular rearrangement. The 4N electron conrotatory ring opening reaction, will give this particular olefin. This olefin, if you include one more of the Pi bond, which is this Pi bond, you can actually create a Hexatriene unit. The Hexatriene unit can undergo, ring closing reaction, to give this bicyclic system, with six membered rings fused together in this particular fashion. Now, all you need to figure out is, the electrocyclic ring closing reaction of the six-electron system, which will undergo electrocyclic ring closing by a disrotatory process. So, if it is a disrotatory process, then we have to move it in the opposite direction.

Let us move this, in the clockwise direction, so that this Hydrogen will go down. This will be anticlockwise direction; the Hydrogen will come up. So, essentially this molecule, which is the E Z Z kind of a Stereochemistry of this triene, will give you the Trans Stereochemistry fusion, has to be Trans with respect to each other, by the disrotatory process of the electrocyclic ring closing reaction, in this particular case.

So, it is again a fairly simple reaction. This reaction, the starting material, the product, as well as the reaction conditions, are very clearly specified. All you have to figure out is, what kind of a molecular rearrangement has taken place, in terms of the skeletal rearrangement, that has taken place. And, what could be the most likely mechanism, that is based on the fact that, Cyclobutene's always undergo ring opening reaction, under thermal condition.

So, you open it up, make a larger ring system, and incorporate one more double bond, so that the six-membered cyclization can take place, to give the bicyclic derivative, which is the six-six fusion. All you have to now figure out is, a Stereochemistry based on the disrotatory ring closing reaction, of this two Hydrogen. What happens to them, during the course of the disrotatory ring closing mechanism.

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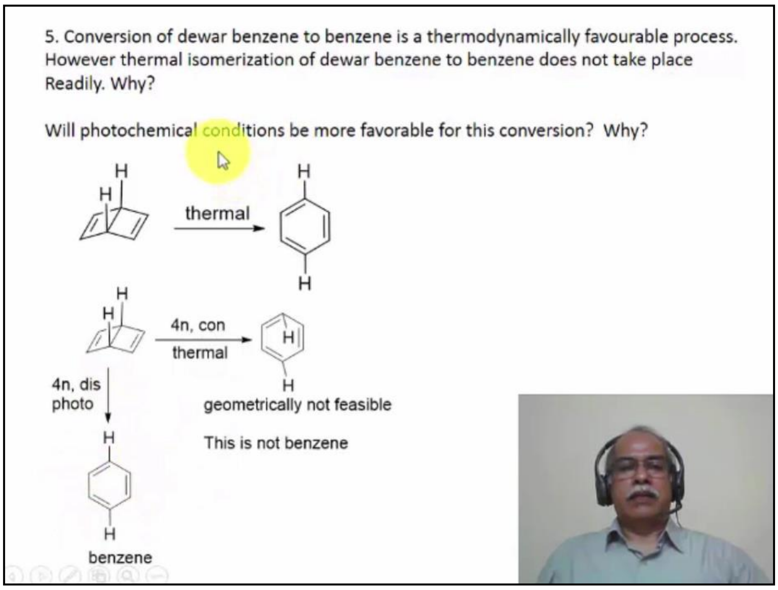

5. Conversion of dewar benzene to benzene is a thermodynamically favourable process. However thermal isomerization of dewar benzene to benzene does not take place Readily. Why?

Will photochemical conditions be more favorable for this conversion? Why?

Now, here is an interesting question. Conversion of dewar Benzene to Benzene, is thermodynamically a favorable process. Because, it gains aromaticity. Dewar Benzene is not aromatic, whereas Benzene is aromatic in nature. So, about 36 kilocalories per mole energy is gained as a resonance energy, in the case of Benzene, which was absent in dewar Benzene. However, the thermal isomerization of the dewar Benzene to Benzene, does not take place readily, why? Will the photochemical conditions, be more favorable for this conversion?

This is something, we have already discussed, during the regular lecture. For example, this is the reaction, that we are talking about. Can you go from the dewar Benzene, which is this bicyclic fused system to a monocyclic aromatic system, which is the Benzene. What happens is, when you do a thermal electrocyclic ring opening reaction, you do not get Benzene at all. You get Trans-Benzene, which is geometrically not feasible.

However, this is because, the conrotatory process will bring one of the Hydrogen in, the other Hydrogen out. So, as a result of that, you get the so-called Trans-Benzene, which is a non-existent molecule. On the other hand, under photo chemical condition, this disrotatory process can put both the Hydrogen out, which will essentially lead to Benzene formation. So, as far as this Transformation is concerned, this is although Woodward-Hoffmann rule allowed by a conrotatory process, it is a geometry forbidden process.

It is not taking place, because the geometry is not feasible. So, although Woodward-Hoffmann rule says that, this would be formed, this is a feasible reaction or allowed reaction, it is Woodward-Hoffmann rule allowed reaction, but geometrically forbidden reaction. On the other hand, the photochemical isomerization is, both the Woodward-Hoffmann rule allowed, as well as the geometry allowed, to give the Benzene. And, that is the answer, for this particular question.

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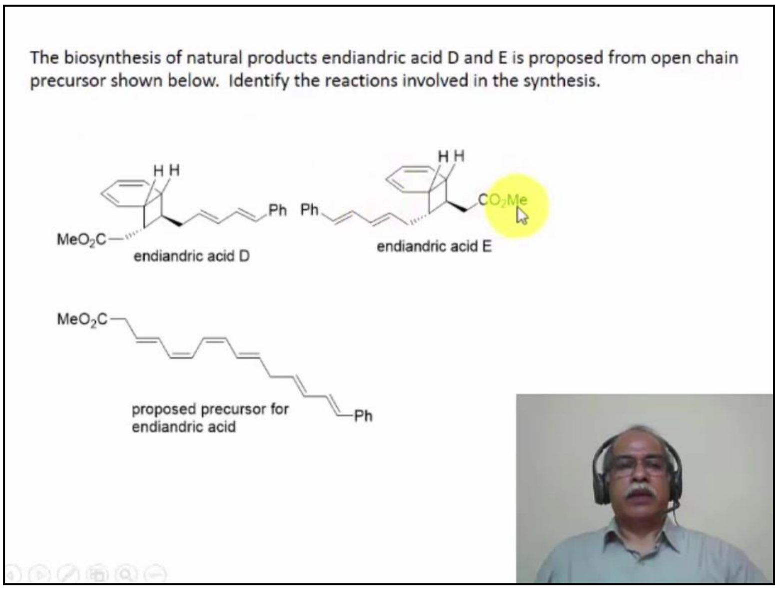

The biosynthesis of natural products endiandric acid D and E is proposed from open chain precursor shown below. Identify the reactions involved in the synthesis.

Now, these are some natural product structures are given. These are called Endiandric acid D and E. So, this is Endiandric acid-D. And, this is Endiandric acid-E. And, these are bio, these are natural products. So, somebody has proposed a biosynthesis, for the formation of this natural products in nature. And, the precursor, that is suggested is, this particular precursor, which is an acyclic open chain precursor. Now, all you have to do is, from this precursor, how do you get this Endiandric acid D and E, by means of a cyclization process.

Now, identify the reaction involved in the synthesis of this two molecules, starting from this open chain molecule, that is given here. Now, what is important to recognize is that, the CH 2 C O O M E group, which is present here. CH 2 C O O M E group, that is intact. And, this diene portion, that is C double bond C, C double bond C phenyl, that is also being present. So, these end terminal groups are not involved in the reaction. They just behave like a substituent, on this particular polyene system. What is the polyene system. This is 2 +2+2+2 8 electron system, is what we have.

So, it is a octa tetraene molecule. The octa tetraene molecules are known to undergo electrocyclic ring closing reactions, to give Cyclooctatriene molecules. The Cyclooctatriene molecules are further known to undergo, electrocyclic ring closure reaction, to give this fused bicyclic system, which is a 6,2 fusion. In other words, six membered ring and four membered ring fusion, is what we have in this particular system, constituting the eight carbons, that are arising out of the electrocyclic ring closing reaction, of this octa tetraene.

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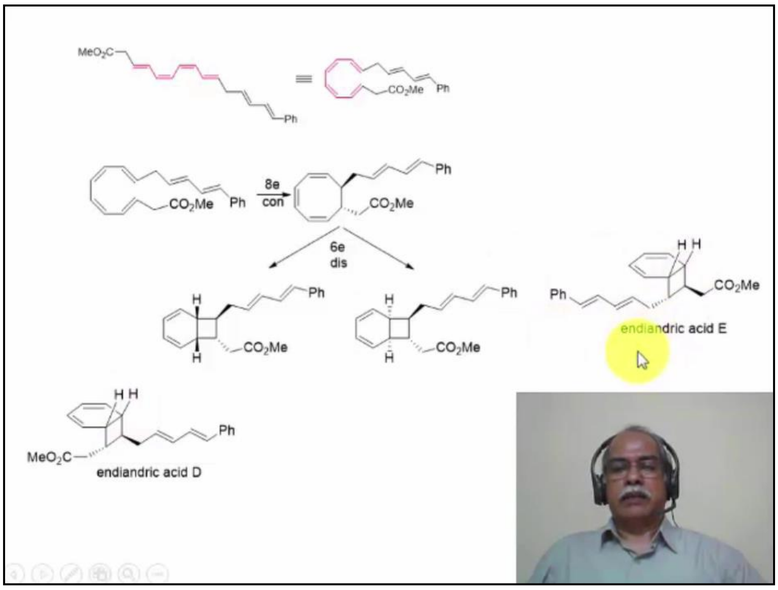

So, the most likely mechanism for this reaction, is the octa tetraene, is written in a zigzag format, in this particular manner. This is a Z double bond. This is also a Z double bond. They can be written in the Z cyclic fashion, in the Cisoid fashion. This is a Transoid confirmation. So, this is a Cisoid confirmation of the same molecule, that is rewritten. So, these are two identical molecules, except this is a conformer of this particular molecule. The conformational changes can take place at high temperatures.

So, once it attains this confirmation, this is the all Cisoid confirmation, which is most favorable condition, for the electrocyclic ring closing reaction to take place. So, one can now do a electrocyclic ring closure, across the carbon number one, and carbon number eight, of this red octa tetraene molecule, that is shown here. That will essentially give you the Cyclooctatriene molecule. The Cyclooctatriene, this is a conrotatory process. So, eight electron system, under thermal condition, it is a conrotatory process, that will bring the two substituents, Trans with respect to each other.

Once the two substituents are Trans with respect to each other, in octatriene system, it can undergo further six electron cyclization, by a disrotatory process. That will put these two Hydrogen, Cis with respect to each other. So, now we have the required Endiandric acid structure, that is shown here. In fact, this structure corresponds to this, where these two Hydrogens, and the pendant vinyl diene group is Cis, with respect to each other. So, they are essentially Cis in the structure also. These two are Trans, with respect to each other.

The ester functional group, and the diene functional group, are Trans with respect to each other. On the other hand, this particular molecule, Endiandric acid-E arises. There are two modes of electrocyclization, that can take place. Both are disrotatory. They can be moving outward, or they can be both moving inward. These are the two possible ways of disrotatory ring closer. If you, for example, take this molecule, and do a electrocyclic ring closure, where you make the arrows inward to the Pi system, the two Hydrogens will come up.

And, that would correspond to this Diastereo Isomer. On the other hand, if you do the arrow movement or twisting movement outwardly, for both the disrotatory process, that will bring the two Hydrogens down. In other words, that will be the Stereo isomer. These two are Diastereo Isomers, with respect to each other. And, the Endiandric acid-E and Endiandric-D’s formation can be explained, by the two possible modes of electrocyclization. Both are disrotatory process only.

The disrotatory process can be, both moving inward or both arrows moving outward, in terms of twisting of this particular carbon-carbon bonds, in this molecule. So, the explanation is that, the acyclic system has to first to adopt a Cisoid geometry, so that cyclization is feasible. Once the Cisoid geometry is formed, cyclization occurs. First, a conrotatory process in eight electron system, followed by a six electron disrotatory process, to give the bicyclic system.

And, those are the structures, that are actually belonging to the Endiandric acid E and D molecule.

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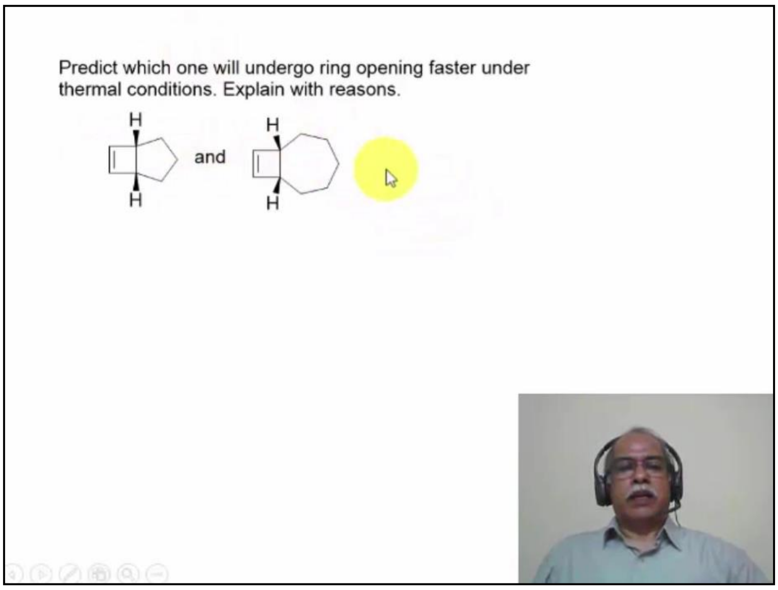

Predict which one will undergo ring opening faster under thermal conditions. Explain with reasons.

Now, i leave you with the problem to think about. These are two molecules. This is a molecule, where you have a four-membered fused to a five-membered ring, is a Cis Stereochemistry. In this case, here four membered ring is fused to a seven-membered ring, with the Cis fusion, in this particular case. The question is, ready to which one of will undergo, faster reaction, ring opening reaction, under thermal condition. So, the clue is given, that is electrocyclic ring opening reaction. And, the clue is also given that, it occurs under thermal condition.

All you need to do is, find a reason, suitable reason to explain, which. First of all, you have to predict, which one will react faster. And then, give an explanation as to, why the one that you are picked, is reacting faster than the other one. So, think about it. And see, the answer can be found in one of the lecture notes itself, where this problem has been already discussed. Hopefully, this problem-solving session will be very useful for you, to understand the certain basic concepts.

And, also reaffirm the fact that, the Woodward-Hoffmann rules can be strictly followed, in most of the electrocyclic reactions, that we discussed in this case, which is actually telling you, whether it is an allowed reaction or a forbidden reaction. It is not only telling you the prediction of whether the reaction is allowed or not, it also predicts the Stereochemistry of the ring junctions, properly. So, this kind of a problem-solving session will be essentially useful, to understand the basic concepts. Thank you very much, for your kind attention.