Pericyclic Reactions and Organic Photochemistry

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Module No. #05
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Pericyclic Reactions – Chelotropic reactions – Introduction SO2 extrusion reactions

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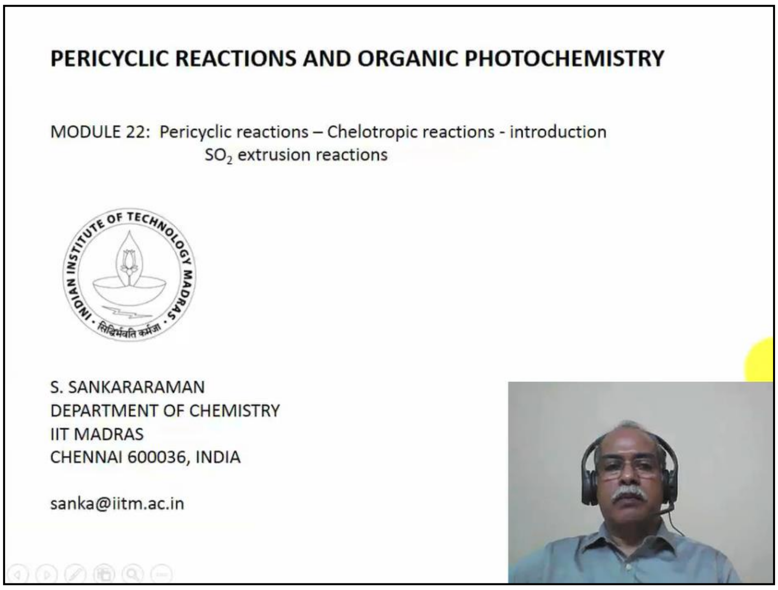

PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

MODULE 22: Pericyclic reactions – Chelotropic reactions - introduction
SO_2 extrusion reactions

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Hello, welcome to the online course on, Pericyclic Reactions and Organic Photochemistry. This is Module Twenty-Two, of this particular course. And, in this Module, we will consider Chelotropic reaction. Particularly, Chelotropic reactions involving, Sulphur dioxide extrusion reactions. In other words, reactions in which, Sulphur dioxide is eliminated as a neutral molecule, during the course of the reaction.

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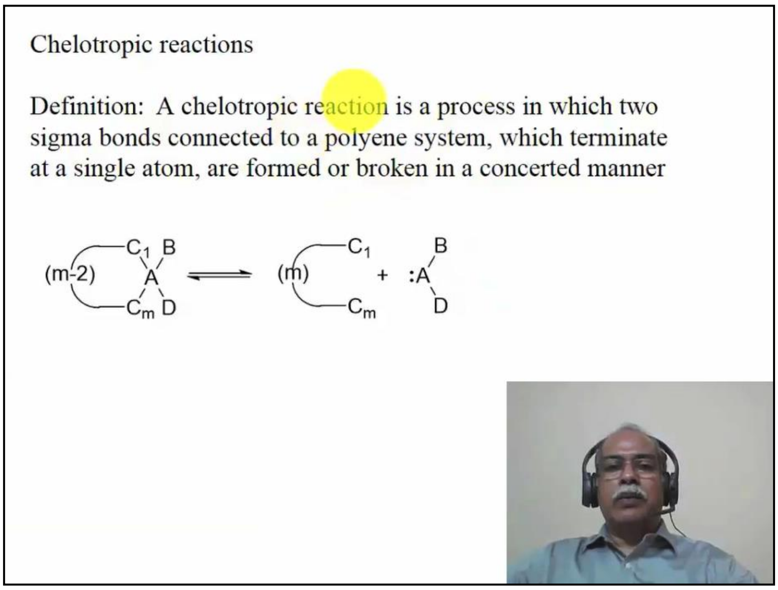

Chelotropic reactions

Definition: A chelotropic reaction is a process in which two sigma bonds connected to a polyene system, which terminate at a single atom, are formed or broken in a concerted manner

Now, the definition of Chelotropic reaction is given, in this particular slide. A Chelotropic reaction is a process, in which, 2-Sigma bonds are broken, which are originally connected to a Polyene system. You consider, this molecule, here. This is a Polyene system, consisting of M-2 number of PI bonds, involved in the cyclic system. Now, C1A and CMA are the 2-Sigma bonds, that are originally connected to Atom A, with the Cyclic Polyene system. And, the C1A bond and the CMA bond are broken, releasing the molecule, which is DAB.

So, the neutral molecule, which is DAB, is released in this particular reaction, resulting in the formation of a Polyene system, which is Acyclic Polyene system now, containing M number of PI electron. There are 2PI electrons, more than the starting material, because of the electrons coming from the breaking of the C1A and the CMA bond. So, i hope, this schematic tells you much more clearly, what a Chelotropic reaction is. Chelotropic reactions are reactions involving, elimination of neutral molecules like, Nitrogen, Sulphur dioxide, Carbon dioxide, Carbon monoxide, and so on.

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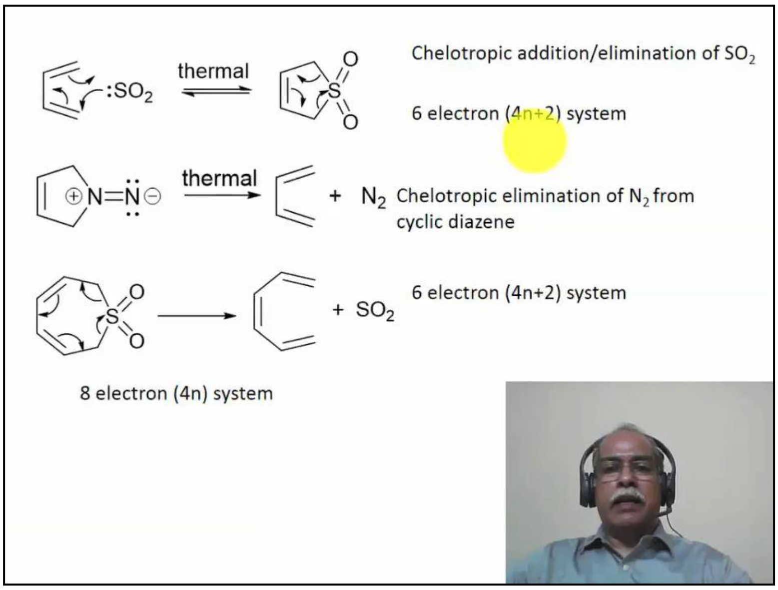

Chelotropic addition/elimination of SO_2

6 electron (4n+2) system

Chelotropic elimination of N_2 from cyclic diazene

6 electron (4n+2) system

8 electron (4n) system

Now, the Chelotropic reactions can be analyzed, in many ways. Now, let us first consider, the examples of Chelotropic reaction. Here is a reaction of Butadiene, reacting with Sulphur dioxide, resulting in the formation of the Sulfolene, as the product, which is this particular product. The reverse reaction, is the extrusion of Sulphur dioxide, to give Sulphur dioxide and Butadiene, as the product. This is a reversible reaction. This reaction was essentially discovered, during the study of the vulcanization of rubber, using Sulphur, as the cross-linking agent.

Sulphur dioxide is invariably produced, at high temperatures, in the presence of Oxygen. And, the scientist, who was investigating in Dunlop Laboratory, essentially discovered this particular reaction, involving the addition of Sulphur dioxide to Isoprene, or the elimination of Sulphur dioxide from the Isoprenyl adduct of the Sulfolene derivative, the corresponding Sulfolene derivative from Isoprene. So, this particular reaction, essentially involves a 4N+2 number of electrons.

In other words, 6-Electrons are involved, as you can count from the number of arrows, that are shifted in the transition state structure, in this particular case. So, the 6-Electrons that are involved, are the 2PI electrons, and the 4-Sigma electrons. 2-Sigma electron, connecting this Carbon and Sulphur, and 2-Sigma electron connecting this Carbon, and this particular Sulphur, in this particular instance. Now, Cyclic-Diazene’s also undergo, thermal elimination of Nitrogen molecule.

One neutral molecule of Nitrogen is eliminated, by same mechanism, as it is shown here, for example, resulting in the formation of Butadiene. But, once Nitrogen is formed, the reaction is not a reversible reaction. The top reaction is reversible. It is in the forward direction, it is possible, if you have a high pressure of Sulphur dioxide. In the reverse reaction, it is possible at high temperature, the continuous removal of the Sulphur dioxide.

The equilibrium can be shifted in the forward direction, using high-pressure of Sulphur dioxide. And, in the reverse direction, by the continuous removal of Sulphur dioxide, that is formed. Unlike, the top reaction, the Nitrogen extrusion reaction, is not a reversible reaction. Nitrogen, once it is formed, it is unreactive. It does not further react with the Butadiene, to give back the starting material.

Similarly, in this particular case, this is a higher homolog of the first reaction, that is shown. This reaction involves, 8-Electrons in the system. As you can see, the number of arrows, that are counted here are, four arrows are counted. So, 4 times 2, 8-Electrons are involved in the reaction.

4PI electrons, which are these 2PI electron, and these 2PI electron. And, 4-Sigma electron, two of the Sigma electron, and two of the Sigma electrons, are involved, during the course of the Chelotropic elimination of Sulphur dioxide. Once the Sulphur dioxide are eliminated, the reverse reaction is, does not take place, for example. So, this reaction is also not a reversible reaction, involving 8-Electron system, in this case.

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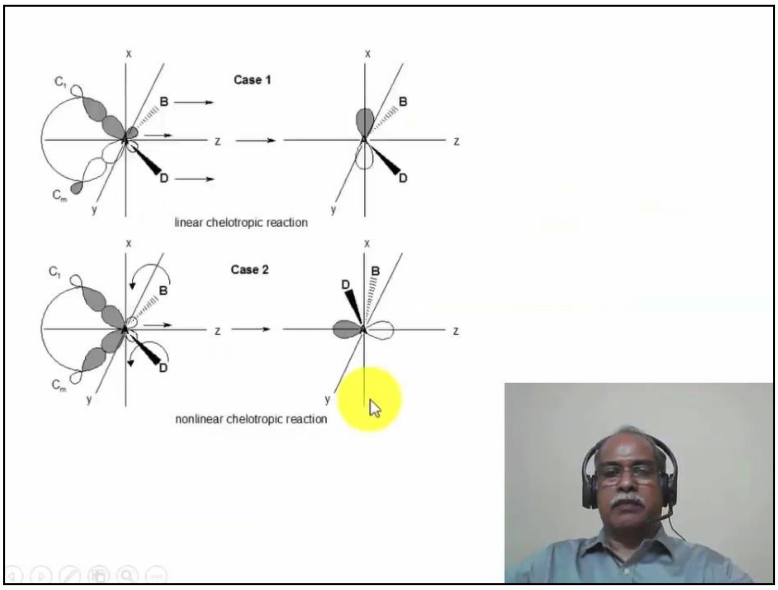

The way to analyze, the Chelotropic reaction. There are two types of transition state, that are involved in a Chelotropic reaction. One is called the, Linear Chelotropic reaction. Other one is called the, Non-Linear Chelotropic reaction. In the Linear Chelotropic reaction, the molecule, which is a Cyclic Polyene molecule containing the molecule, that is going to be eliminated, namely DAB molecule, is confined in a cartesian coordinate, such that, the Atom A occupies the origin, and Atom B and D essentially lie in the YZ plane, of this particular system.

So, you can see here, in this Chelotropic reaction, the B and D are pulled along the direction of the Z, resulting in the formation of the DAB molecule, by the cleavage of the C1A, and the CMA bond. These two bonds are cleaved, during the course of the reaction, resulting in the formation of a P-Orbital on the Atom A, along the direction of the X-axis. In the case of the, Non-Linear Chelotropic reaction, this is a Non-Linear Chelotropic reaction.

Because, Atom B and Atom D are pulled upward, towards the X-axis. So much, so that, at the end of the reaction, the DAB molecule is actually lying on the XY plane, not on the XZ plane. So, as a result of that, there is a tilting motion that is taking place, as shown by these curved arrows, resulting in the formation of a P-Orbital, along the Z direction. So, this is a Non-Linear Chelotropic reaction, and this is a Linear Chelotropic tropic reaction.

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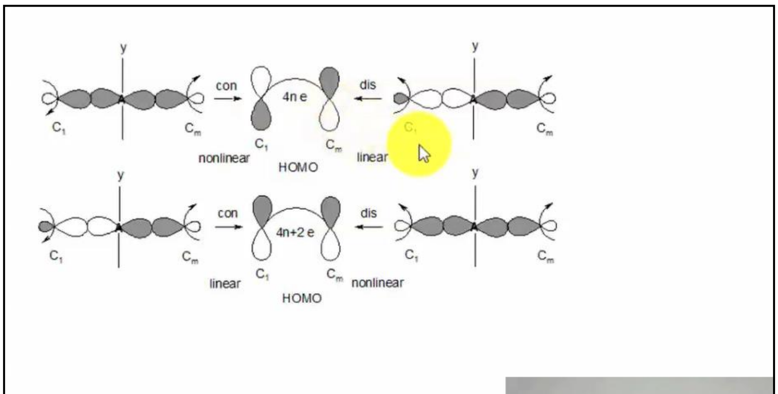

One can use the, Frontier Molecular Orbital analysis kind of a system, to consider the Non-Linear, and the Linear Chelotropic reaction, and derive the Woodward-Hoffmann rule, in terms of Conrotatory and Disrotatory process, that can take place, during the cleavage of the Sulfolene kind of a molecule.

Now, if you consider the Homo of the Non-Linear system, or the Linear system, as the case maybe. This is a Symmetrical combination of the molecular orbital, in the Non-Linear system. Whereas, this is anti-Symmetrical combination of the molecular orbital, in the Linear system. This undergoes a Disrotatory process, essentially to produce this Homo of the molecule, that is shown here. So, this is essentially an allowed process.

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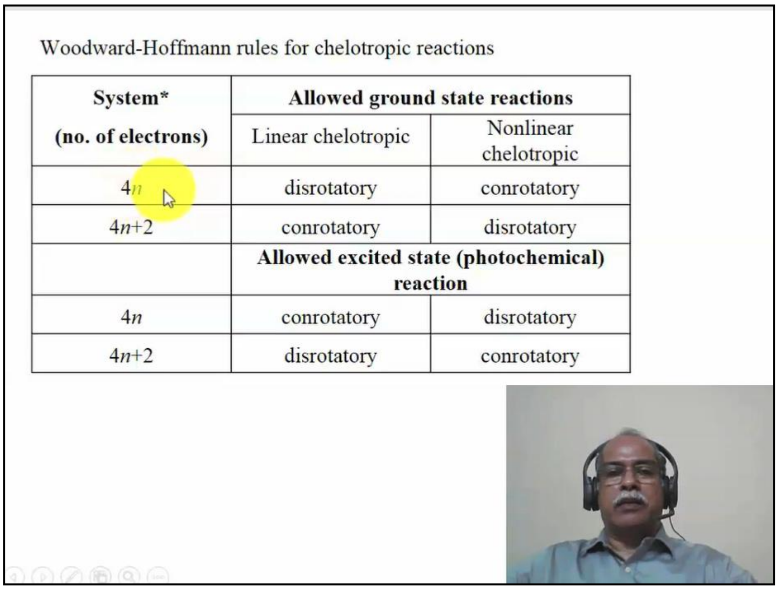

Woodward-Hoffmann rules for chelotropic reactions

System* (no. of electrons)	**Allowed ground state reactions**	
	Linear chelotropic	Nonlinear chelotropic
4n	disrotatory	conrotatory
4n+2	conrotatory	disrotatory
	Allowed excited state (photochemical) reaction	
4n	conrotatory	disrotatory
4n+2	disrotatory	conrotatory

If you consider, the Woodward-Hoffmann rules, this is a 4N electron system. If it is a 4N electron system, then it is an allowed process, in the ground state. In other words, under thermal condition, by a Disrotatory process for the Linear, and Conrotatory process for a Non-Linear.

So, Disrotatory process Linear, this is an allowed process. Conrotatory process, Non-Linear also, is an allowed process, if it is a 4N electron system. If it is a 4N +2 electron system, then the Non-Linear process, will have the Disrotatory process.

Whereas, the Linear process, will have the Conrotatory process, which are allowed, which are complementary to each other.

So, under the thermal condition, it is very clear, 4N electron system will undergo Disrotatory motion, whereas a 4N +2 electron motion will undergo the Conrotatory process, for Linear Chelotropic reaction. In the Non-Linear Chelotropic reaction, it will be just the opposite. Under Photochemical condition, it is complementary to the Thermal reaction.

When it is allowed Disrotatory manner, for a 4N electron system, then it is allowed in the Conrotatory manner, for the 4N electron system, under Photochemical condition.

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So, these are the Woodward-Hoffmann rules, essentially derived from the FMO kind of an analysis, which is shown in this particular slide. And, the results are interpreted, in this manner.

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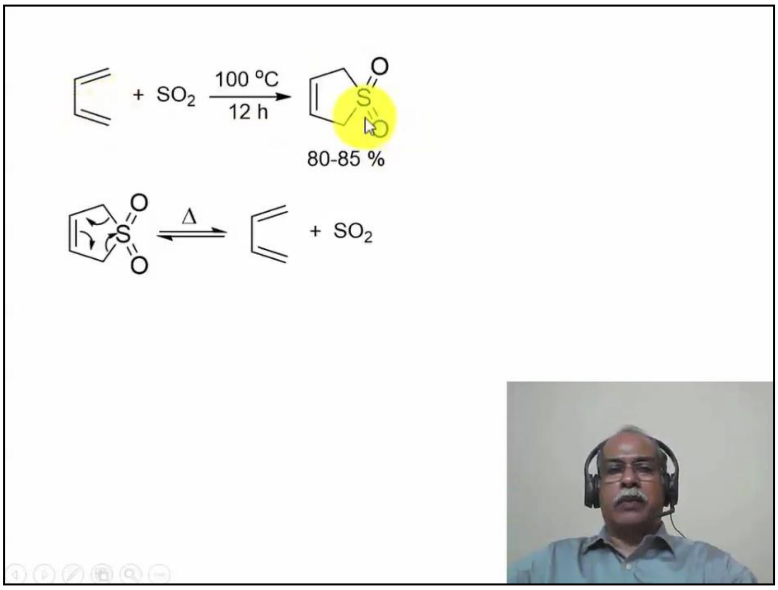

As mentioned earlier, Sulphur dioxide can react with the Butadiene, at a high temperature, and high pressure, resulting in the formation of Sulfolene. Sulfolene can undergo decomposition, to give Sulphur dioxide, and Butadiene also. So, depends on, how the reaction is pushed. If the high-pressure of Sulphur dioxide use, then it can be pushed on the left-hand side direction. If Sulphur dioxide is continuously removed, then it can be pushed in the right-hand direction also. One should see this reaction as a, method of storing Butadiene, which is a gas, in the solid form.

This Sulfolene is a solid material. So, once solid material is heated, you form the gaseous product. So, whenever Butadiene is needed, for a Diels-Alder kind of a reaction, one can also take the Sulfolene, and heat it up. In-situ, generate the Butadiene. And, trap the Butadiene with another dienophile, resulting in the formation of a Diels-Alder adduct. We will see, some examples of such a reaction, in due course. So, essentially, one can consider this as a solid equivalent of Butadiene, which can be thermalized, to give the Butadiene quite readily, by elimination of Sulphur dioxide.

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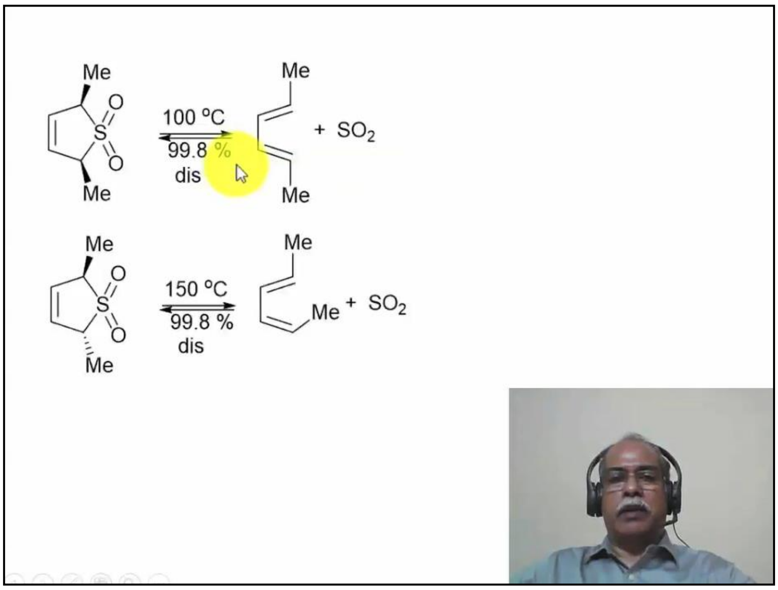

The reactions are, highly Diastereoselective in nature. If you consider the Cis isomer of the Dimethyl substituted Sulfolene. In other words, 2,5-Dimethyl substituted Sulfolene, is what we are talking about. In the forward direction, it undergoes a Disrotatory motion of these two bonds namely, this Carbon-Sulphur bond, and this Carbon-Sulphur bond, resulting in the formation of the two Methyl group being EE isomer of the, Hexa-2,4-Diene is formed, during the course of the reaction.

The reverse reaction also, if you take the Hexa-2,4-Diene, EE isomer and U-Sulphur dioxide as a trapping agent, the Sulfolene that is formed, is a Cis Dimethyl Sulfolene, that is formed. If you take the other Diastereo isomer, namely the Trans Dimethyl substituted Sulfolene, it undergoes decomposition at higher temperature, again in a very highly stereoselective manner, it produces a EZ isomer.

The EZ isomer of a Hexa-2,4-Diene, when it is treated with Sulphur dioxide, the reverse reaction takes place, resulting in the formation of the Trans. In all these cases, this is a Disrotatory process, that is allowed. And, that is what happens, in this particular case. So, if you look at this reaction, the 4N+2-Electron system reaction, the Disrotatory process is formed. So, it has to be a Non-Linear Chelotropic reaction kind of a system, is what we are taking.

This is a 6-Electron system, involving 2PI electrons here, 2-Sigma electrons, and 2-Sigma electrons, overall it is a 6-Electron system. So, it is a 4N +2 system. 4N +2 system, under thermal conditions, when it undergoes a Disrotatory process, it is clearly a Non-Linear Chelotropic kind of a reaction.

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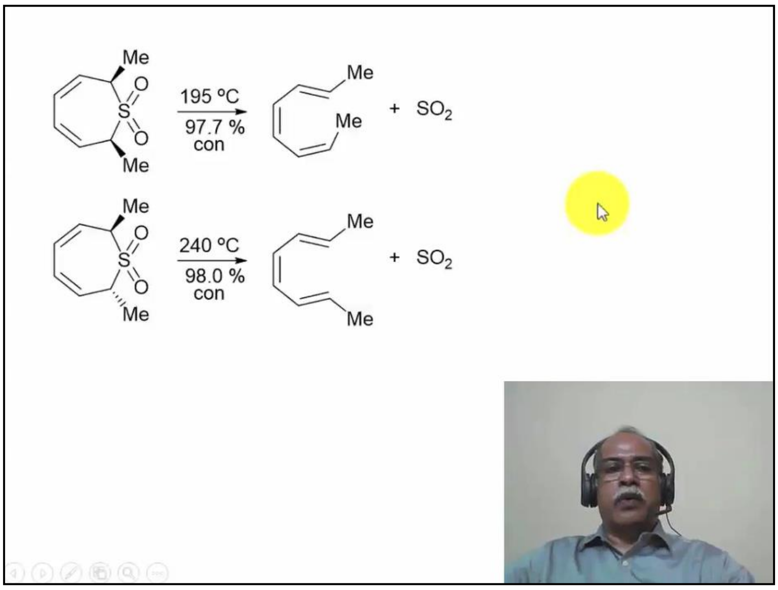

If you go to the higher order system, the higher homolog of the system, Sulphur dioxide extrusion is the process, that takes place, in a highly Diastereo selective manner. The Cis isomer here, gives the EZZ isomer of the Octatriene molecule. Octa-2,4,6-Triene molecule, is what we are getting, in this particular case. On the other hand, the reverse reaction is not possible. This is occurring, by a Conrotatory process.

A Conrotatory process involving, a twisting of this Carbon Sulphur bond, and this particular Carbon Sulphur bond, resulting in the formation of this particular product. On the other hand, if you take the Trans Dimethyl derivative of the higher homolog, which is shown here, in the bottom, that undergoes the decomposition at higher temperature, again in a highly Diastereo selective manner, resulting in the formation of the EZE isomer of the Octatriene product, which is this particular product, in this case.

So, the reactions are highly Diastereo selective. They undergo, either in a Disrotatory fashion, or Conrotatory fashion. If you see, the Disrotatory process for a 4N plus electron system, this is very similar to the Electrocyclic selection rule, or Electrocyclic Woodward-Hoffmann rule. In the Electrocyclic reactions also, a 4N+2 reaction, under thermal condition, will be Disrotatory favored.

A 4N electron system, will be Conrotatory favored, a 4N +2 electron system, will be Disrotatory favored, essentially correlating the Electrocyclic reaction, to the Chelotropic reaction, by means of a Woodward-Hoffmann rule. Whatever the Electrocyclic reaction Woodward-Hoffmann rule, applies to the Chelotropic reactions also, in this particular manner.

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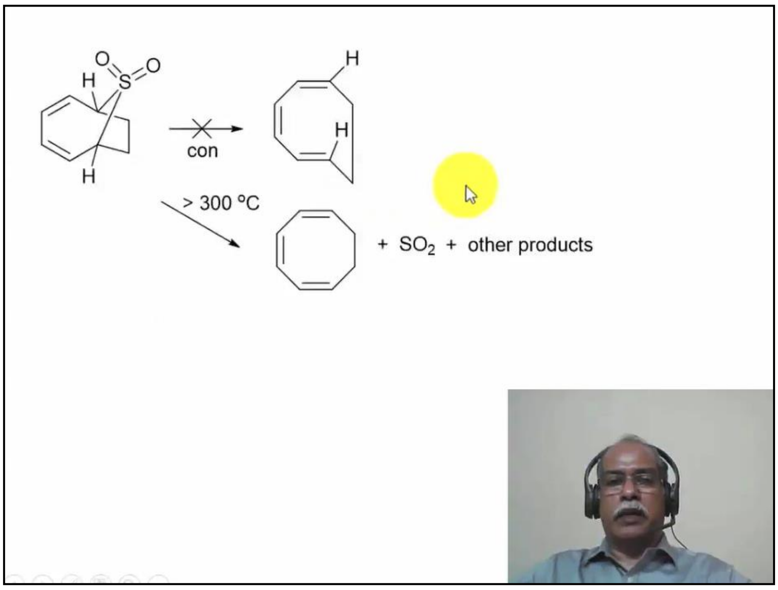

Now, this molecule, which is a bicyclic Sulfone molecule, undergoes extrusion of Sulphur dioxide, at a very high temperature of 300 degrees, perhaps involving a non-concerted pathway, involving stepwise breaking of the Sulphur-Carbon bond. The reason being that, if it is a Conrotatory process, it would involve the formation of a Trans Cyclooctene kind of a products. Octatriene kind of a product, which is not a geometrically favorable system.

So, the Conrotatory process, which is a symmetry allowed process, does not take place readily. At higher temperature, a non-concerted pathway, is what is proposed for the formation of the Cyclooctatriene, in this particular instance. So, this is not a Sigmatropic reaction. This is a Chelotropic reaction. This is a Non-Concerted Chelotropic reaction. As, the Concerted Chelotropic reaction is not viable, because of the formation of a Trans double bond, in the product.

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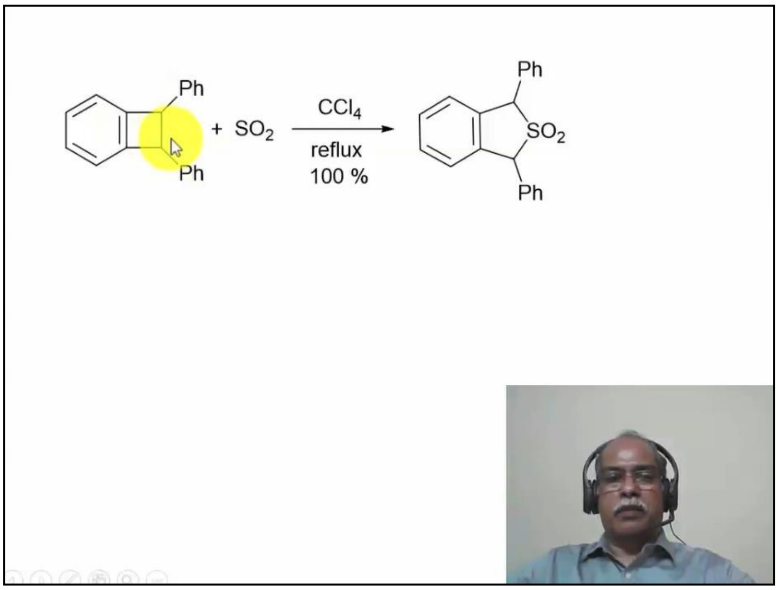

Here is an example of the Sulphur dioxide, trapping an Ortho Quinodimethide kind of a system. The Benzcyclobutene on heating, will give the ring opening, resulting in the formation of Ortho Quinodimethide. This is an Electrocyclic reaction, which we have already studied, in the Electrocyclic chapter.

So, the Quinodimethide intermediate that is formed, is trapped by Sulphur dioxide, to produce the Ben Sulfolene, as the product. This is in fact, a very efficient process for trapping of the Ortho Quinodimethide derivative, that is obtained from the thermolysis of the Benzcyclobutene, resulting in the formation of a product, which is shown on the right-hand side.

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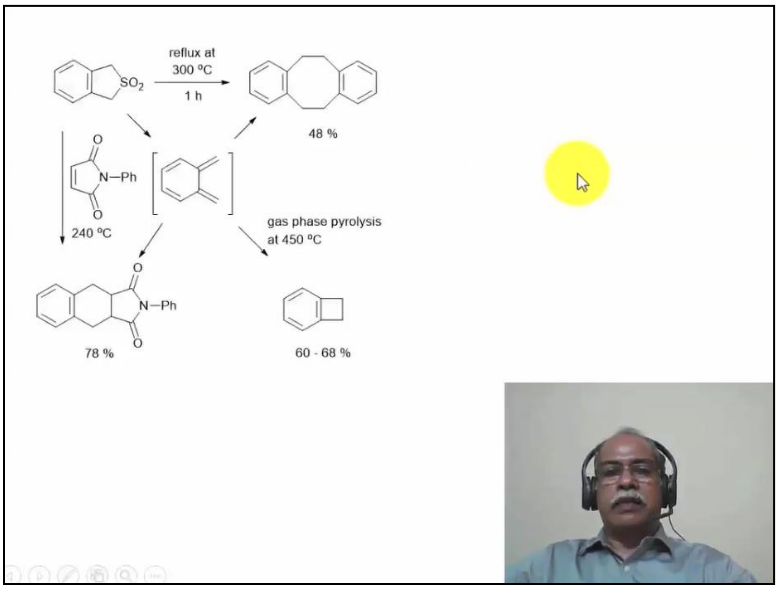


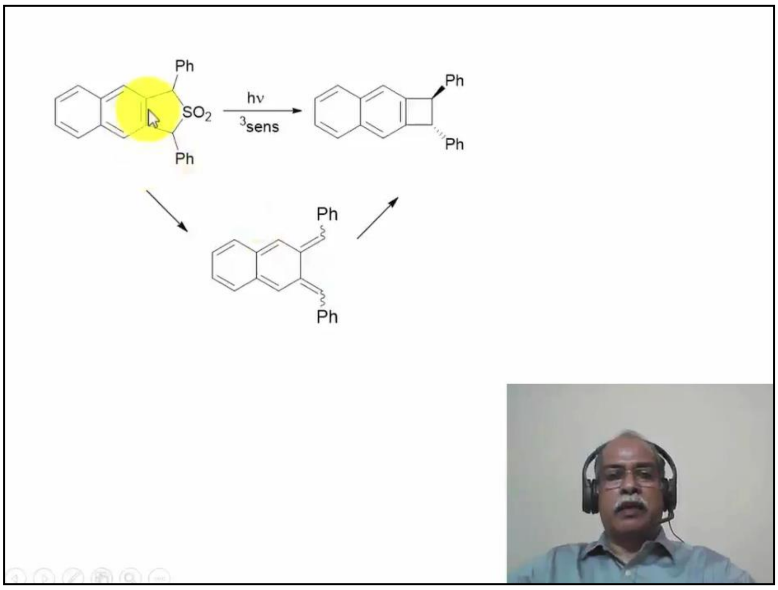
The reverse reaction, has been studied by Cava. The reverse reaction is that, if you take the Ben Sulfolene, and heat it up to high temperature of 300° Celsius, it forms Ortho

Quinodimethide. In the absence of any trapping agent, the Ortho Quinodimethide, essentially undergoes a 4PI-4PI Cycloaddition reaction, resulting probably not a concerted pathway, is a stepwise pathway probably, resulting in the formation of the Dibenzo Cyclooctadiene kind of a molecule, which is shown here, obtained in 48% yield.

In the presence of a trapping agent like, the N-Phenylsuccinimide, for example, this molecule, undergoes the Diels-Alder reaction, with N-Methylsuccinimide, resulting in the formation of the cycloadduct, in 78% yield. If it is not done in the solution phase, if it is done in the gas phase pyrolysis at high temperatures, the Ortho Quinodimethide that is formed, undergoes ring closing reaction, to give the Cyclobutene.

In fact, the Cyclobutene will undergo ring close essentially, this is a gas phase reaction, through a flow system probably, where the Benzcyclobutene is trapped, which cannot further undergo decomposition, to the Ortho Quinodimethide, in a reversible manner. So, this is probably a Flash Vacuum Pyrolysis kind of an experiment, where the Benzcyclobutene is trapped in liquid Nitrogen trap, under the gas phase, resulting in the formation of about 68% of the product, with the reverse reaction of this particular.

This reaction is a forward reaction. Whereas, this is a reverse reaction. From the Benzcyclobutene, you go to the sulfolene, in this case. Whereas, from the sulfolene, you go to the Benzcyclobutene, in this particular case.



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Here is a higher homolog of a Naphthalene system, undergoing the Chelotropic elimination of Sulphur dioxide, to give the corresponding Quinodimethide. The Quinodimethide, under the Photochemical condition, essentially forms a Trans Diphenyl isomer of the Naphtho

Cyclobutene. Just like Benzcyclobutene, this is Naphtho Cyclobutene kind of a molecule. Diphenyl substituted Naphtho Cyclobutene, is what is formed, in this reaction.

This is an intermediate, that is proposed. Unfortunately, the stereochemical information of the ring opening, is not known. It is only the ring closing product, that is known. And, since, it is a Conrotatory process, this is probably a ZE isomer, is what is undergoing the ring closing reaction, to give the Trans Diphenyl derivative, as one would expect in this case.

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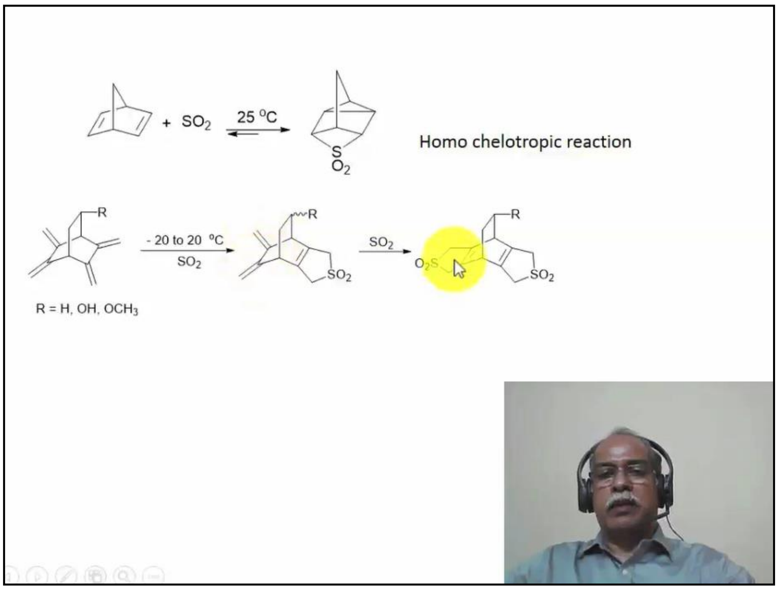

Homo chelotropic reaction

R = H, OH, OCH$_3$

Norbornadiene, undergoes a very unusual Chelotropic kind of a trapping. When the high pressure of Sulphur dioxide is used, Norbornadiene reacts in a Homo Chelotropic reaction. This is considered as a Homo Chelotropic reaction. The reaction essentially take place, because of the two proximity of this particular bonds, which is inwardly oriented P-Orbitals are present in the system.

We have already seen this, in the 2+2 Cycloaddition reaction, which gives Quadricyclane from the Norbornadiene. Here, it undergoes a Sulphur dioxide inclusion, between these two positions, with the concomitant formation, of a Carbon-Carbon bond formation, in the backside, which is this particular Carbon-Carbon bond, that is being formed. So, this reaction essentially takes place, at room temperature.

When this molecule is heated, it will undergo reversibly exclusion of Sulphur dioxide, from the cyclic adduct, that is formed, in the forward reaction. In the case of Tetra Exomethylene 2,2,2-Bicyclic system, at low temperature, when it is treated with Sulphur dioxide, a Bis trapping is what is taking place, with the Sulphur dioxide.

The Bis Sulfolene is formed essentially, as the product of the reaction, of this Tetra Methylene 2,2,2-Bicyclic system. First reaction is, Sulphur dioxide trapping, using this two

Methylene units, which is a Exomethylene group, resulting in the formation of the Sulfolene. The second molecule is also trapping this particular Exomethylene derivative, forming the Sulfolene derivative, from the other side of the molecule.

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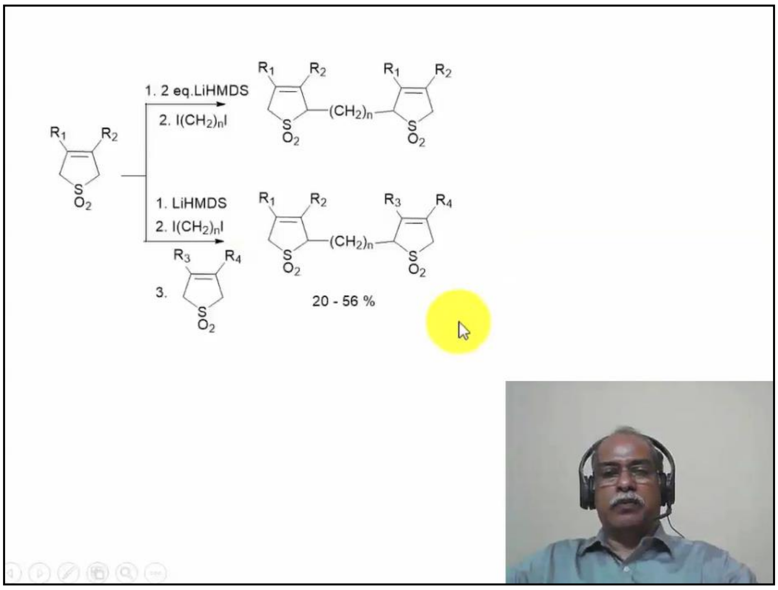

The synthetic utility of the Sulphur dioxide, capturing by the Butadiene, is what is illustrated in this particular example. The Alpha protons of the Sulfolene, are highly acidic in nature. And, they can be deprotonated, by treating with the Lithium Hexamethyldisilazane, or Butyllithium kind of a reagent. So, once the Carbanion is generated, that is nucleophilic in nature. And, that reacts in an SN2 fashion, with this Diiodo compound, to give the Methylene bridged Bis Sulfolene derivative, which is this particular derivative.

You can have the same Sulfolene reacting, to give this particular molecule, that is shown here. Alternatively, it can also give with another Sulfolene molecule, after the generation of a Carbanion here, you treat it with the one mole of the Iodide, to just mono substituted derivative. Repeat the same process, with a different Sulfolene, then you get a different Sulfolene, attached to this. So, it is possible to make, both Symmetrical, as well as Unsymmetrical, Methylene bridged Sulfolene derivatives, of this kind.

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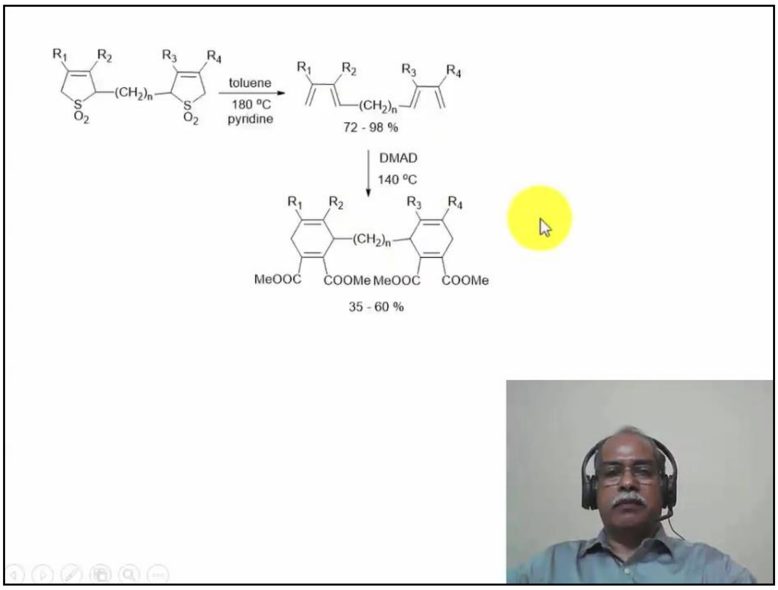

What is the use of this derivatives? When they are heated in Toluene, in the presence of Pyridine, Pyridine is essentially to trap the Sulphur dioxide molecule. You regenerate the Butadiene units from the system, which are separated by a Methylene linker. The Methylene linker chain can be varied, depending upon the Diiodo derivative, that is being taken for the synthesis.

Once the Butadiene molecules are produced, they can be trapped with Dimethyl Acetylene Dicarboxylate, which is abbreviated as DMAD, in this particular case, by a Diels-Alder reaction. A double Diels-Alder reaction, essentially produces this Hexadiene unit, which could be a synthetically a very valuable intermediate, in many synthesis.

Because, one can take this Dihydro Aromatic derivative, and aromatize them, by treating with the DDQ, resulting in the formation of an Aromatic system, that is linked by a Carbon Methylene chain, for example, containing the Ester functional groups, in this particular case.

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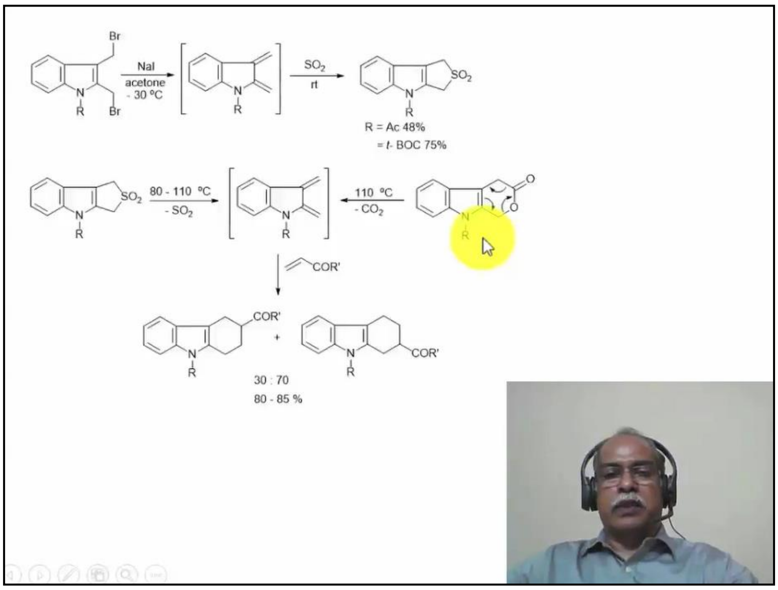

The Sulphur dioxide trapping of the Ortho Quinodimethide kind of a derivative, is also used for the synthesis of this kind of derivatives, which are carbazole derivatives. How are they synthesized? You take the Dibromo derivative, and treat it with Sodium Iodide, a 1,4-Elimination takes place, resulting in the formation of a Exomethylene Ortho Quinodimethide kind of a derivatives. So, an Indole Ortho Quinodimethide derivative, is what is formed here.

In the presence of Sulphur dioxide, it is trapped at -30°, for example, resulting in the formation of the Sulfolene, which is actually fuse to the Indole kind of a derivative. This can be used, to regenerate the Ortho Quinodimethide derivative, by simply heating. So, this is kind of a storing, this reactive intermediate, in a Sulfolene form. As and when, it is needed, this Sulfolene can be taken, and it can be heated, to form the intermediate, which was originally produced. That can be trapped, by a different type of Diels-Alder Dienophiles.

In this particular case, Ethyl Vinyl Ketone, is what is taken. And, it undergoes the Diels-Alder reaction, in a Regio selective manner, to give this two products, in 30:70 ratio, this being the major product, in this particular case. So, this is essentially used for the synthesis of Carbazole derivatives of this kind. The Ortho Quinodimethide of the Indole, can also be synthesized, by heating this particular Lactone. Carbon dioxide is eliminated in this process, to give this particular derivative.

So, what we have seen in this module, is essentially an introduction to Chelotropic reaction. There are two types of Chelotropic reaction. The one, involving a Linear Chelotropic reaction. The other one, involving a Non-Linear Chelotropic reaction. The diagram essentially, clearly defines, what is a Linear, and what is a Non-Linear, Chelotropic reaction. Then, we looked at several examples of Sulphur dioxide inclusion, as well as Sulphur dioxide exclusion reactions, from Sulfolene kind of a molecule.

And, some synthetic applications of the Chelotropic reaction, involving Sulphur dioxide, is also illustrated, in this particular module. I hope, you enjoyed this module. Thank you very much, for your attention.