Pericyclic Reactions and Organic Photochemistry

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Module No. #06
Lecture No. #28
Photochemistry of Alkenes – Cis-Trans Isomerization

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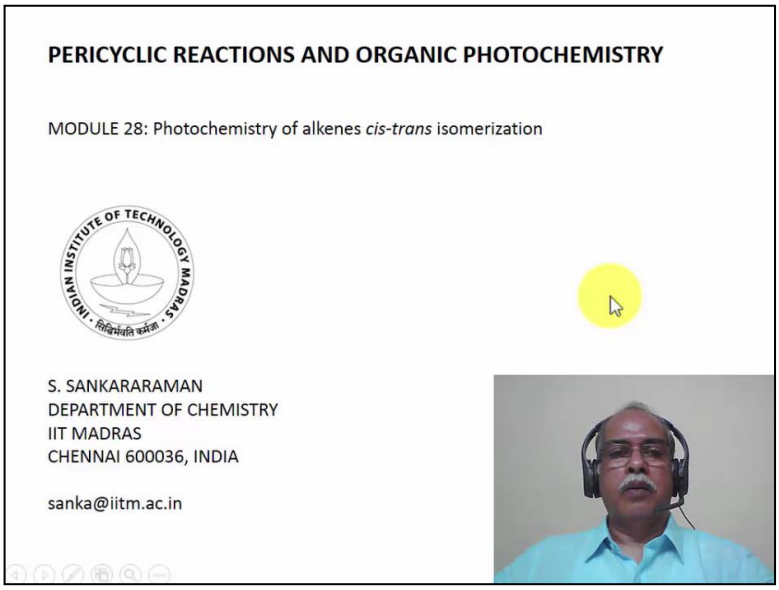

Hello, welcome back to the online course on, Pericyclic Reactions and Organic Photochemistry. We are now in, Module Twenty-Eight, of this program. In this Module, we will concern ourselves with the Photochemistry of Alkenes, particularly the Cis-Trans isomerization of Alkenes.

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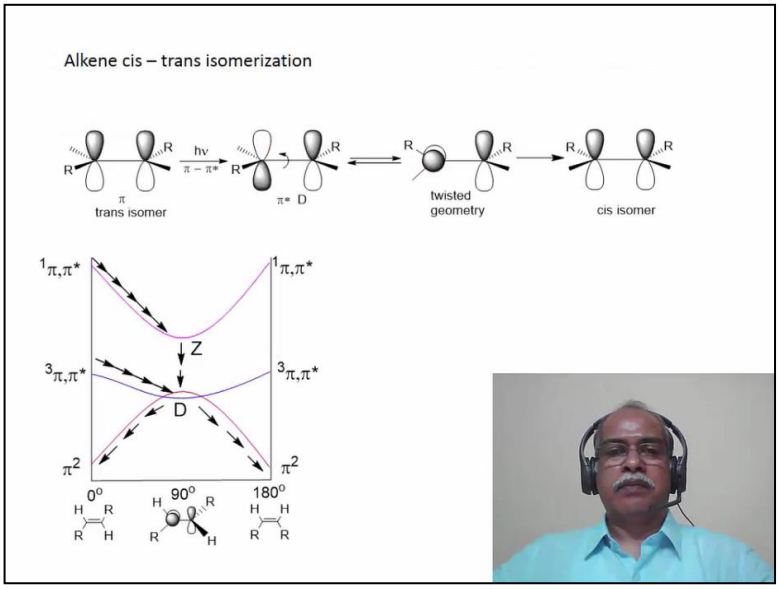

Now, as you know, the conversion of the Trans-Alkene to a Cis-Alkene, or a Cis-Alkene to Trans-Alkene, cannot be promoted by Thermal activation. It has to be done, only under Photochemical activation. The bond rotational activation barrier, is typically 40 to 60 Kilocalories per mole, for the rotation of the double-bond, in an Olefin. Therefore, Thermal energy is not available at room temperature, or high temperature, to cross over the barrier, for the Cis-Trans isomerization process, to take place.

Now, how is it happening, in the case of Photochemical Cis-Trans isomerization. If you consider, the Trans isomer of the Olefin, which is shown here, with the Homo-orbital, that is shown clearly, upon PI to PI-Star excitation, you go to the Lumo level, one of the electron is excited to the Lumo level. So, this would be the PI-Star level. The PI-Star level has a Diradical kind of a state, in which, it exists. And, as a result of that, the bond order is reduced to one. Because, now you have 1-Electron in the PI bond, and 1-Electron in the PI-Star bond.

So, the net bond order, is reduced to one. Now, the reduced bond order, allows the Carbon-Carbon bond, to freely rotate, such that, the twisted geometry can be obtained, by a simple rotation of the Carbon-Carbon bond, in the excited state. Once the twisted geometry is obtained, it can go back to the Trans isomer, or it can go forward it to the Cis isomer. And, this is the generally accepted mechanism, for the Cis-Trans isomerization of Olefin. From the energetics point of view, one can consider the Cis-Trans isomerization, using this particular diagram.

On the X-axis, the angle of twist, is what is plotted. This is a Trans geometry. This is a twisted 90° geometry, where the two lobes of the P-orbitals, are perpendicular to each other. Then, you have the 180 degree, which is corresponding to the Cis isomer, in this particular case. Now, one can go from the Trans isomer, to the Cis isomer, provided, if the molecule

crosses this activation barrier, which is roughly 40 to 60 Kilocalories per mole. This is not possible to do so, under Thermal condition.

However, under Photochemical condition, one can excite the Olefin directly, to the PI-Star level, which would be a Singlet PI-Star level. From the Singlet PI-Star level, one can funnel down to the transition state, of the Cis-Trans isomerization. Or, in other words, from the PI-Star excited state, one can come to this twisted geometry, that is shown here. From the twisted geometry, of course, one can go either to the Trans isomer, or to the Cis isomer, with certain probabilities.

Now, one can also do the Triplet sensitization mediated, Cis-Trans isomerization. A sensitizer, absorbs the energy, and transfers the energy, to the Triplet state of the Olefin. So that, the Triplet PI to PI-Star state of the Olefin, is populated. That is also, higher in energy, compared to the activation barrier, or the transition state of the, Cis-Trans isomerization process. So, from there also it can come down to the, transition state of the Cis-Trans isomer.

This twisted geometry, can be obtained. From there, one can go to, either Trans isomer, or the Cis isomer, as the case may be. So, this simple diagram essentially, explains the process of Cis-Trans isomerization, from the point of view of energies of the Ground electronic state, the excited PI-Star electronic state, which is in the Singlet state, or in the excited PI-Star electronic state, which is the Triplet state, of the Cis-Trans isomers.

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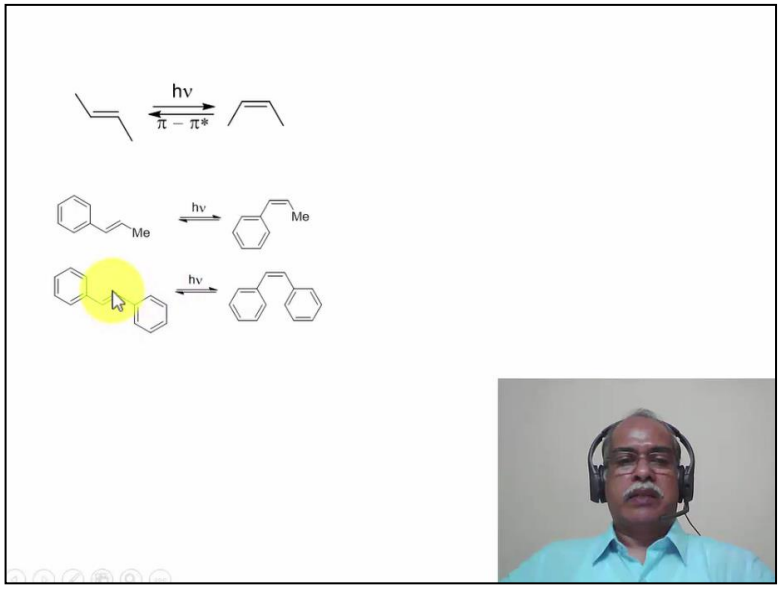

Now, these are some examples of Cis-Trans isomer. Trans-Stilbene can be, photochemically isomerize to the Cis-Stilbene. In fact, the Trans-Stilbene- Cis-Stilbene Photoisomerization, will attain an equilibrium. And, it will eventually attain a Photostationary state.

Photostationary state is, when two systems like the Cis and Trans, are in equilibrium with continuous photolysis, certain constant population of the Cis and Trans isomer, is obtained.

At the Photostationary state, there is a conversion from, the Cis to the Trans, and the Trans to the Cis, in equal rates of reaction, for example. And, thereby, it reaches a steady-state population, which is called the Photostationary state. Here is an example of a Methyl Styrene, undergoing Cis-Trans isomerization.

Here, Trans-Stilbene is undergoing, Cis-Trans isomerization to Cis-Stilbene. One can photochemically, spectroscopically, characterize the Trans-Stilbene, and the Cis-Stilbene, because they have independent existence. So, from the UV-visible spectra, one can easily distinguish, the Cis-Stilbene, and the Trans-Stilbene, quite readily.

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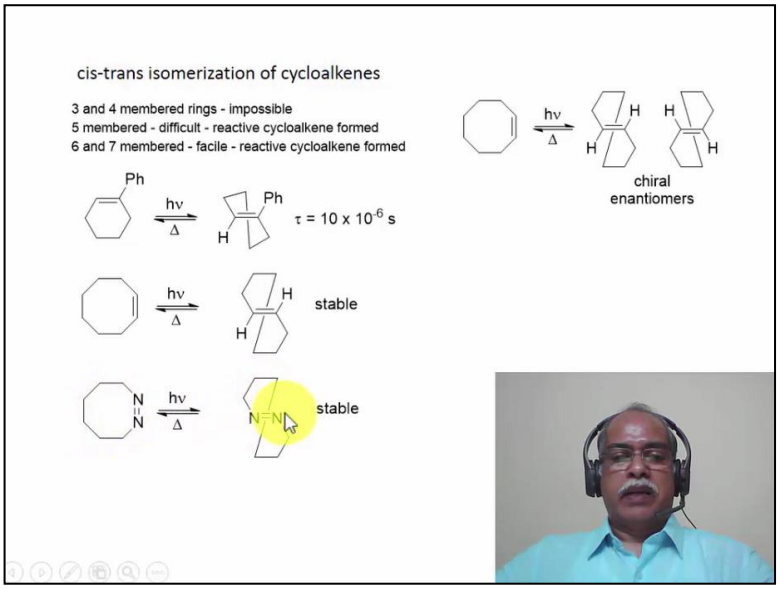

Now, in the case of Cyclic Alkenes, remember, the simple Cyclic Alkenes like the 3-Membered, 4-Membered, and 5-Membered, cannot accommodate a Trans double-bond, because of the constraint geometry. So, from the 3-Membered to 4-Membered, it is almost impossible to get the Trans isomer. 5-Membered, with difficulty, one can obtain the Trans isomer. However, it is a very reactive intermediate, that is formed.

It does not have a sufficient lifetime, to be isolated. The 6-Membered, 7-Membered, there is a Facile Trans isomer, that is formed. For example, if you take the Phenyl Cyclohexene, it can undergo the Cis-Trans isomerization, from the Cis isomer to the Trans isomer. The Trans isomer has a lifetime of about, 10 Microsecond or so. Under Thermal condition, it goes back to the Cis isomer.

On the other hand, if you take Trans octane, which is a larger ring system, it undergoes Cis-Trans isomerization. The Trans isomer is quite stable. In fact, the Trans isomer is a Chiral

molecule. It will form an Enantiomeric mixture, of this two structures, which are shown here. These two structures, do not have any kind of a symmetry. They have a C2 symmetry, but that is not sufficient condition, for the Achirality.

So, this is a Chiral molecule, with non-super imposable mirror image, is what is shown here. And, one can do the isomerization, using a circularly Polarized light, equivalent to an Asymmetric synthesis. Because, remember, circularly Polarized light, is a Chiral light. So, when you use a Chiral light, to do this isomerization, one can induce Asymmetry, and generate one Enantiomer, of the Chiral Trans Cyclooctene.

Now, this is a Cyclic-Azo compound. The Cyclic-Azo compound, is in the Cisoid form. Cis configuration, here. It undergoes, Photochemical isomerization to the Trans isomer. Because, again, this is an 8-Membered ring system, the Trans isomer is stable. Under Thermal condition, it slowly undergoes the isomerization, back to the Cis isomer, in this case.

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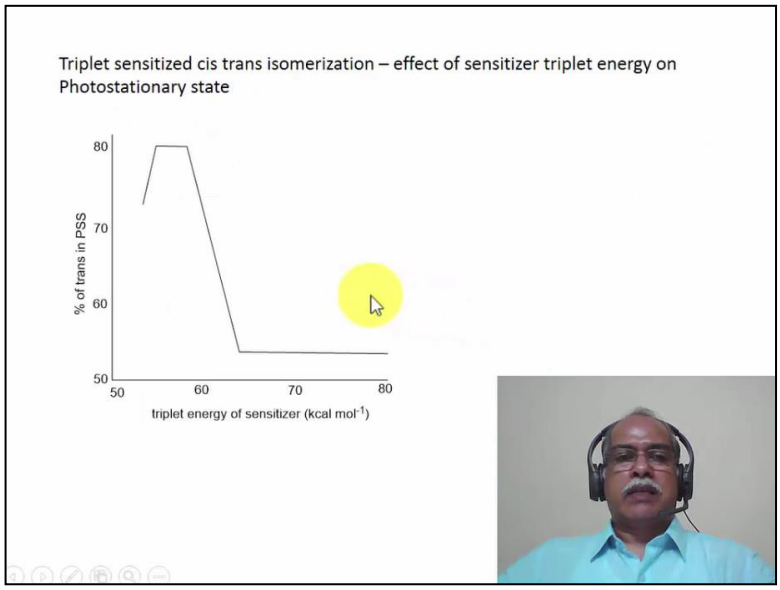

Now, this diagram essentially explains, the concentration or the Cis-Trans ratio, under Photostationary state, with respect to the Triplet sensitizer energy. Remember, a molecule, which is capable of undergoing a Triplet sensitization, can observe the photon energy, go to its Triplet state. From its Triplet state, it can transfer the energy, to the Triplet state of the Alkene. Then, the Alkene can proceed, to undergo the Cis-Trans isomerization.

In other words, this is the process by which, it will undergo Cis-Trans isomerization. From the ground state, it gets excited to the Triplet state, by sensitization process, not by direct absorption of light. And, after it is sensitized, it funnelsed down to the Diradical state, which is the twisted Diradical state. And, the Diradical can, either go to the Cis isomer, or the Trans isomer.

In order, for such a mechanism to operate, there are certain conditions, with reference to the Triplet energy of this molecule, a sensitizer. So, in the X-axis, we have plotted the Triplet energy of the sensitizer. And, in the Y-axis, the percentage Trans isomer in the photo station. PSS essentially means, Photostationary state. Photostationary state is an equilibrium state, in which the concentration of the Trans isomer, is plotted here.

Now, we can see here, with the Triplet energy of the sensitizer, being around 65 or so. Above 65, both the Cis isomer, as well as the Trans isomers, are sensitized. So, they have a roughly equal population about, 55:45 ratio of the population, is what they have.

So, as a result of that, nearly 1:1 mixture of the Photostationary state, is what is prevalent in this energy regime. As you decrease the Triplet sensitizer energy, it seems, only the Cis isomer is getting converted, into the Trans isomer. Because, the percentage of Trans isomer is getting more and more, in this particular case. This is because of the fact that, the Trans isomer Triplet energy, is much higher than the Cis Isomer-Cis Triplet energy.

So, sensitization selectively occurs, only to the Cis isomer, in producing the Trans isomer, in this particular instance, for example. It goes, up to the level of about 80% of the Trans isomer, in the Photostationary state. And then, there is a small fall, when the Triplet energy goes below, 55 Kilocalorie per mole, or so. So, this diagram essentially explains the, effect of the Triplet energy of the sensitizer, to the Photostationary state equilibrium concentration of Cis and Trans isomers, in a Photoisomerization process.

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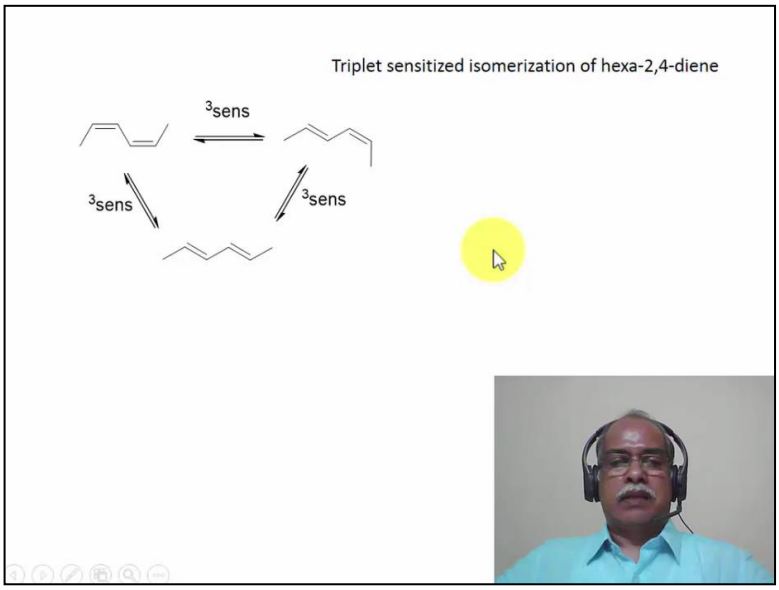

Dienes can also be, Photoisomerize to the Trans isomer. Here is a Cis-Cis isomer of Hexadiene, Hexa-2,4-Diene. Hexa-2,4-Diene, under Triplet sensitized condition, can undergo, for example, a stepwise process. Initially, it can undergo, 1-Cis double-bond can be isomerized, to the Trans double-bond. Then, both the double-bond can be isomerized, to the Trans double-bond.

So, this is a ZZ isomer. And, this is a EE isomer. And, this can be equilibrated, depending upon the stability, and depending upon the sensitizer energy, one can reach a Photostationary state, of all these three isomers. This is ZZ, ZE, and EE isomer can be, Photostationary state can be obtained.

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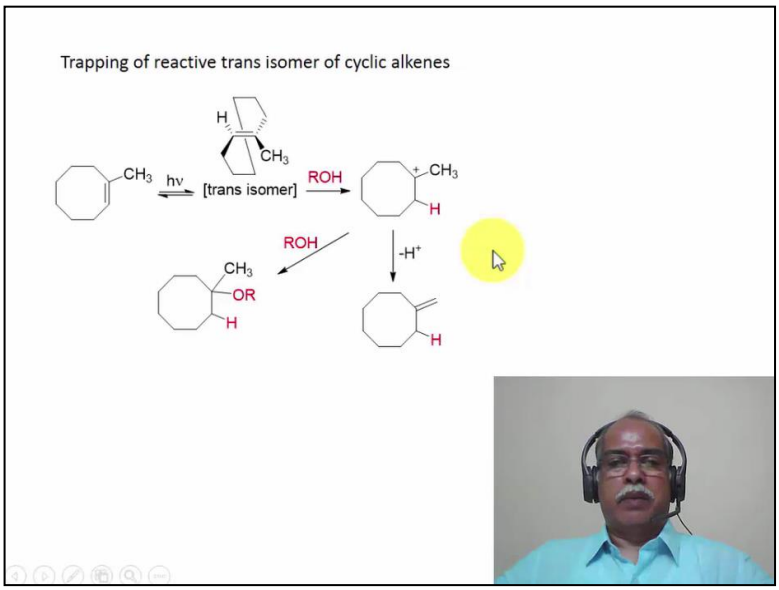

When the isomerization of a Trans Cis-Octene takes place, to go to the Trans-Octene, the Trans-Octene, although it is a stable molecule, it is fairly reactive molecule, because there is still some strain, associated with the Trans geometry of the 8-Membered ring, so much so that, it can react with the solvent, it can be trapped with a solvent. When alcohol is used as a solvent. The alcohol protonates the double-bond, to generate a Carbonium ion.

The Carbonium Ion can, either lose a proton from the side chain, to give the Exomethylene compound, which is an isomer of the starting material. Or, it can undergo trapping by the Nucleophile, to give the corresponding Ether, where ROH is trapping the cation that is formed, to generate the corresponding Ether. Octile or Ether, is what is formed, in this. This is essentially to show that the Trans isomer, although it is stable and isolable, it is a fairly reactive molecule, compared to the Cis isomer.

The Cis isomer, for example, does not add the alcohol at room temperature. Because, this is an electron rich double-bond. And, ROH is also electron rich, in terms of the lone pairs of electrons, on the Oxygen. So, there must be some kind of a Polarity change, that takes place in the excited state, in the formation of the Trans isomer. This is probably, a more Polar bond, or because the strain is released, it can undergo the protonation, followed by the nucleophilic trapping, in this particular case.

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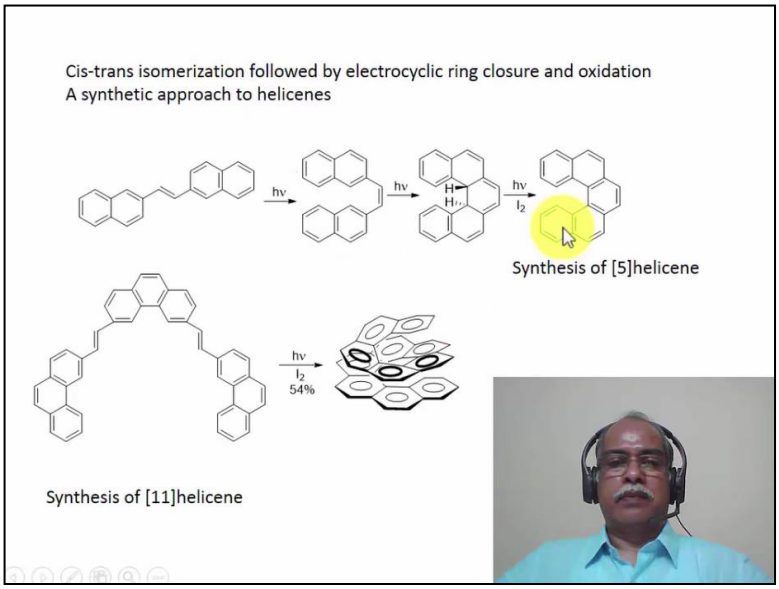

The Cis-Trans isomerization process is put to use, in the synthesis of Helicene. Helicenes are molecules of this type, where you have Benzene rings fused in an angular fashion, to complete the circle, for example. Here is an example of a [11] Helicene. There are 11-Benzene ring, which are fused in an angular fashion. So, it forms a helical structure. After the

sixth fusion, angular fusion for example, it will bump into this particular ring. If you fuse, another 6-Membered ring over here, that will essentially bump into this ring.

So, it will avoid the bumping to this ring, by forming a helical structure. Here is an example of a [11] Helicenes, with 11-Benzene rings, which are angularly fused together, in this particular manner. Now, this class of molecules are Chiral in nature, because of the twist, that is associated with the molecule. They have a helical Chirality. So, they are interesting from the point of view of optical activity, as well as from the structural aspects of this. The simplest Helicene is the, Pentahelicene. This is [5] Helicene.

The Nomenclature is, the number of ring, is given in the square bracket. And, it is thus called Helicenes. [5] Helicene means, there are five rings, which are fused in the angular manner like this, and that corresponds to [5] Helicene. [5] Helicene can be synthesized, by first taking the Beta Naphthyl substituted Ethane. It undergoes Photoisomerization, from the Trans isomer to the Cis isomer. The Cis isomer, remember, this we have already seen in the Electrocyclization reaction.

It undergoes a 6-Electron cyclisation, which is an electrocyclic reaction. It operates in the Conrotatory fashion. Because, 6-Electron cyclisation, under Photochemical condition, will be Conrotatory. So, that puts this two Hydrogens in the Trans position, because of the Conrotatory process. This is a Dihydro Aromatic derivative. Under the Photochemical condition, it can be oxidized by Iodine, to the corresponding Aromatic derivative.

In other words, Iodine radical abstracts one of the Hydrogen, and then the, other Hydrogen is lost simultaneously, with the formation of the unsaturated system, which is the Aromatic system, in this case. If you take a larger ring system, which is Phenanthryl substituted Trans double-bond of this kind. This is a Symmetrical molecule. It can undergo Cis-Trans isomerization. The Cis isomer, will undergo the electrocyclization, twice. Once the electrocyclization, over here. Another electrocyclization, over here.

This is 3+3+3, there are already 9-Benzene rings. Electrocyclization here, will give one more ring 10. And, another electrocyclization here, give one more ring, which is 11. So, [11] Helicene is formed, not in a very bad yield. Actually, 54% yield for a synthesis of this kind, is very decent. Such a fascinating molecule can be synthesized, using the Cis-Trans isomerization process, followed by oxidation of the Dihydro Aromatic system, that is produced.

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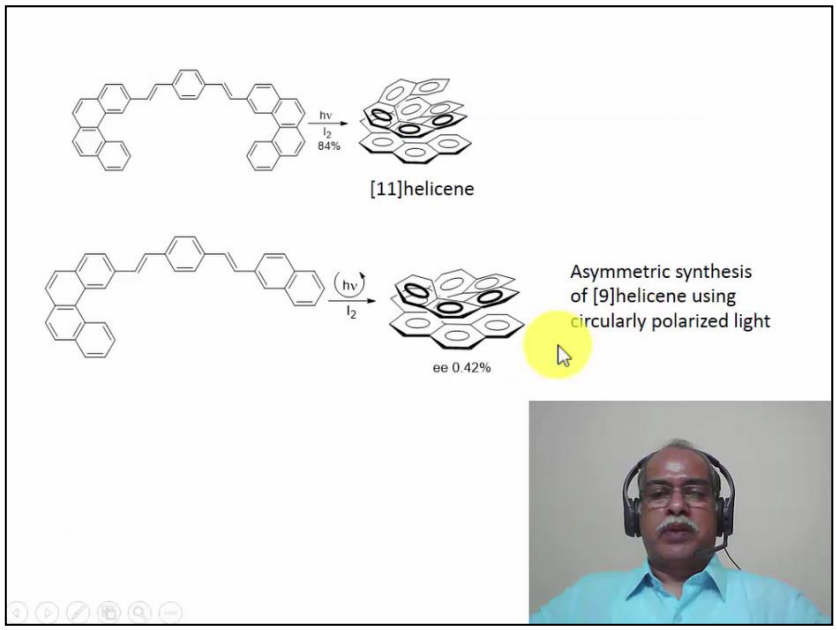

Here is one more example, of the [11] Helicene. In this case, for example, the yield is only 54%. The yield is improved, in this particular case, by taking a larger Helicene. Tetra-4-Helicene is taken here. This is Benz Phenanthrene. This is also Benz Phenanthrene, connected to a Para Phenylene group. This undergoes a Cis-Trans isomerization, followed by oxidative process, to give the [11] Helicene, in this particular case.

Because, Helicenes are optically active, and they are Chiral in nature. If, one uses a circularly Polarized light, under the circularly Polarized light, which is a Chiral light, Asymmetric induction can take place. And, one can produce, Enantiomeric excess of the Helicene, that is formed. Here, the Enantiomeric excess, is not that great. It is only 0.42.

However, a very largest optical rotation, that is exhibited by this molecule. 0.2% Enantiomeric excess, is sufficient to detect, such formation of an optically Pure isomer, because of the high optical rotation, associated with this molecule. Even a very small concentration of one of the Enantiomer, will lead to a big rotation, optical rotation change, in the measurement of optical activity. So, this constitutes an Asymmetric synthesis of the [9] Helicene, using a circularly Polarized light, as an example, is illustrated here.

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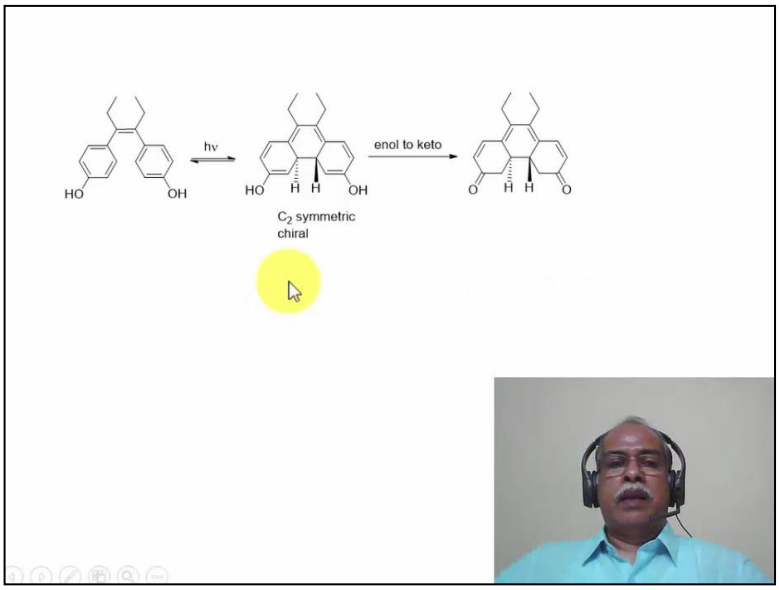

Now, here is another example of the Cis isomer, undergoing the Electrocyclic ring closure reaction. Remember, this molecule is a Chiral molecule. Because, it has only a C2 axis of symmetry. This exist in the Enol form, readily undergoes to the Keto form. The Keto form is also Chiral. It is C2 Symmetric, nevertheless it is a Chiral molecule. The fact that, it is a Chiral molecule, tells us very clearly, the mechanism of the reaction, to be producing the Trans isomer, here.

Because, the Cis isomer will be a Meso isomer. Only the Trans isomer, will be a Chiral isomer. So, stereochemistry can be inferred, from the optical activity, or from the Chirality of the molecule, that is being generated. This is such an example, to illustrate the use of Chirality of the molecule, to deduce the mechanism of the reaction.

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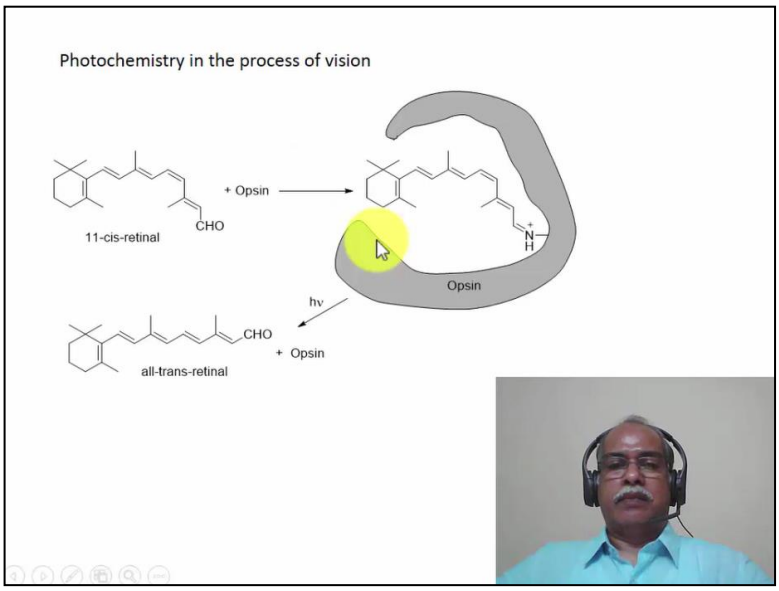

Now, Photochemistry is involved, in the vision process. Essentially, Cis-Trans isomerization is the process, that is responsible for vision from our eyes, for example. The perception of vision, by our eyes. Eyes contain a Protein called Opsin. That is represented, by this cartoonish representation. Opsin Protein has free Amino functional group. This is 11-Cis Retinal. The numbering starts from this Carbon, bearing the Methyl, goes around the ring, like this.

So, this will be 6-7-8-9-10-11. So, this is a 11-position double-bond. This is a Cis Retinal, at the 11 position. It forms a shift base, with the free Amino functional group in the Opsin, which is a Protein. In the active site, which is this pocket, that is shown by a cartoonish representation. Once it is locked, latched on to the Amino functional group, in the form of an Imine, the light causes the Cis-Trans isomerization. The 11-Cis position is isomerized, to the 11-Trans isomer. In other words, you will get the All-Trans Retinal.

Once all Trans Retinal is formed, it is a released in the form of an Aldehyde, and Opsin is regenerated. In the process of Cis-Trans isomerization, although it is a very small structural change, it produces a large conformational change in the Opsin structure, which is recognized as a signal, for the vision process. The signal is sent to the brain, and the brain processes, this as a vision process. So, essentially, when we see something, Cis-Trans isomerization of the Retinal molecule, is what is taking place, in our eyes.

And, this is a nice example of the biological application, of the Cis-Trans isomerization. There is a lot of work, that has gone into the studying, the Cis-Trans isomerization of Retinal molecule, by simple Photochemistry, as well as by time resolved spectroscopy, to identify the chemical species, that are involved in the Cis-Trans isomerization process, of the Retinal molecule, in the eye, which is connected to the Opsin, in the form of an Imine derivative.

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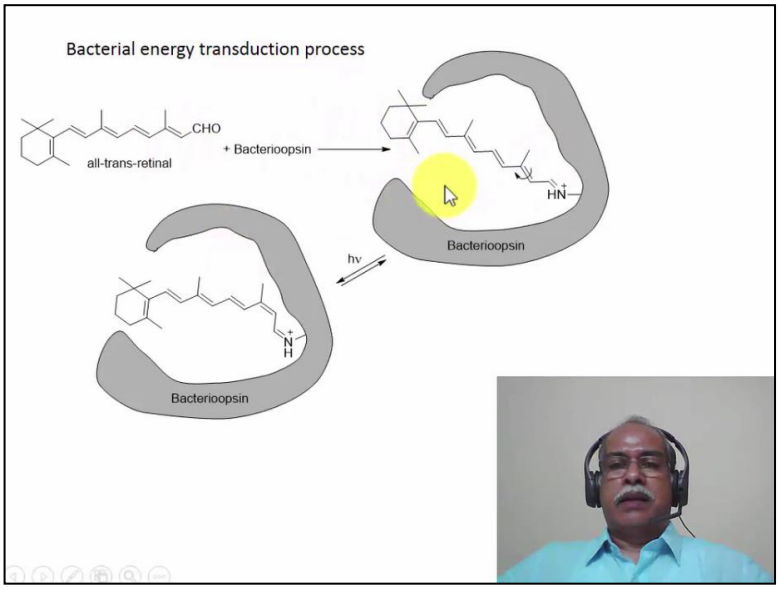

In the case of Bacteria, a similar process takes place, for energy transduction process. In the case of Bacteria, the all Trans Retinal is the one, that is combining with the Bacteria Rhodopsin. The free Amino group, that is in the Bacteria Rhodopsin, forms the Imine. And, in the thirteen position, the Trans double-bond undergoes isomerization, to the Cis double-bond, reversibly. And, this reversible change of the confirmation of the Bacteria Rhodopsin, is taken as a signal, for the energy transduction process.

So, both in the case of Mammals, for the vision process, and in the case of Bacteria, the energy transduction process, the Cis-Trans isomerization processes, essentially the signal, that is responsible for the vision process in Mammals, and in the energy transduction process, in the case of Bacteria.

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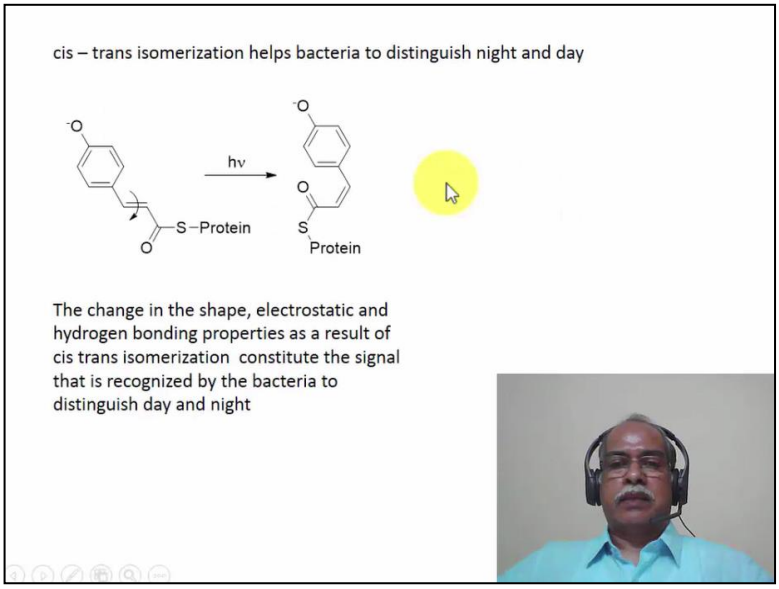

Now, Bacteria's have to distinguish, day from night. They do not have eyes, to see the day and night, in terms of the light energy, that we see during the daytime, and the darkness, that we see in the night time. So, essentially the Cis-Trans isomerization, is acting as a clock, to tell the Bacteria, whether it is a night time, or the daytime. So, it helps the Bacteria, to recognize daylight, and the day and night, for example.

What is the process, that is taking place? A Cinnamic acid ester, Thio ester is formed, with the Protein. The Protein has sulphur Amino acids, which is connected to the Para Hydroxycinnamic derivative. The Anion of the Para Hydroxycinnamic derivative, essentially undergoes a Cis-Trans isomerization. Because of the Cis-Trans isomerization, there is a large change, in the Protein structure.

The secondary structure of Protein is changed. And, that change, causes the change in the shape, change in the electrostatic property, as well as change in the Hydrogen bonding property, of the Protein, which causes a signal, to be recognized by the Bacteria, to distinguish the day and the night. So, this is a very nice way of trying to identify, whether it is a daytime or nighttime, by a simple Photochemical process.

If this process is taking place, for example, it would be taking place, only during the daytime, because you need photon energy. If, this process is shut off, for example, then it would be night, as recognized by the Bacteria, because of the large signal changes, that it perceives, because of the Protein conformation change.

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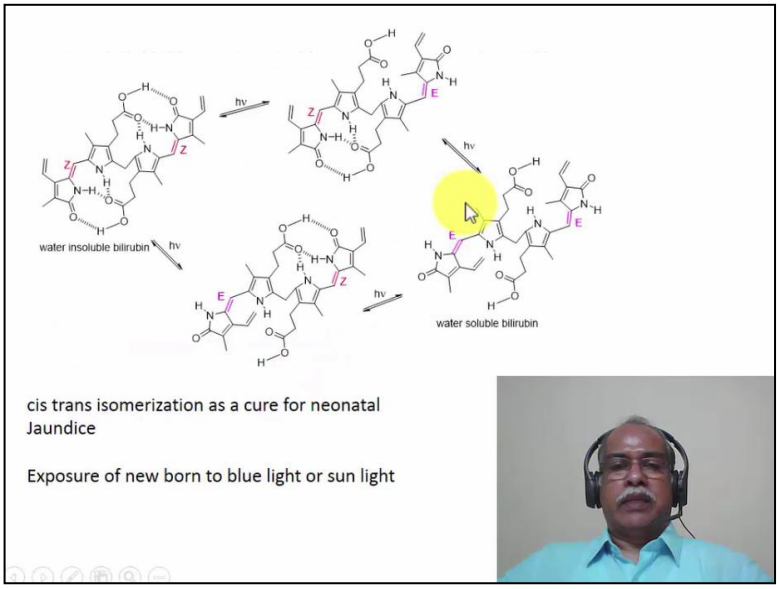

Now, some Babies are born with Jaundice, which is known as the Neonatal Jaundice. This is caused by the molecule called Bilirubin. Bilirubin, is this particular molecule. You can see here, Bilirubin has two Cis double bonds, which are indicated in the Red, as Z double bonds, in this particular structure. Because, it is in the Z geometry, it is in a favorable geometry, to have Hydrogen bonding interaction, like this. The Hydrogen bonded structure, is highly Hydrophobic in nature.

So, it essentially become a precipitate. It is a water insoluble molecule, in terms of this particular configuration, of the Cis double-bond here, and Cis double-bond here, which brings this Amide functional group, in proximity to the Carboxylic acid functional group, to undergo the Hydrogen bonding interaction. So, this is a highly Hydrophobic, because of the Hydrogen bonding interaction, it is highly Hydrophobic. The Carboxylic acid functional group, the Amide functional groups, are tied together.

So, it becomes an insoluble material. It accumulates under the skin, and in other organs of the body, for example, which causes the Neonatal Jaundice. That is one of the reason, why Babies, who are born with a Neonatal Jaundice, are put under the Blue light, so that, the Photoisomerization, of the Cis-Trans isomerization, can be promoted. What is the use of the Cis-Trans isomerization, in this particular process.

See for example, when this undergoes the isomerization, from the Z isomer to the E isomer, the E isomer has a totally a different configuration here. The Amide functional group, is not pointing towards the, Carboxylic acid functional groups. So, the Hydrogen bonds are completely broken. This Polar group is exposed, now. This Polar group is also exposed. Similarly, the other Z double-bond can be isomerized, to the E double-bond. The same effect, takes place. All this Hydrogen bonds get broken, in the Cis-Trans isomerization process.

When, both the Z isomers are isomerized, to the E isomer, there is no longer any Hydrogen bond. This is a highly Polar molecule. This is a water-soluble molecule. So, it does not get precipitated. And, the Cis-Trans isomerization process, is essentially the cure for the Neonatal Jaundice of New-Born Babies. That is why, new born Babies are sometime exposed to the Blue light, or Sunlight.

In India, for example, the Babies, who are born with a Neonatal Jaundice, sometimes, we put them out, in the sunlight, just to get this process going, namely the Cis-Trans isomerization of the Bilirubin. One is a water insoluble molecule, which is responsible for the Jaundice. Whereas, other one is a water-soluble molecule, which can be excreted through urine, and other processes, and thereby curing the Neonatal Jaundice of New-Born Babies.

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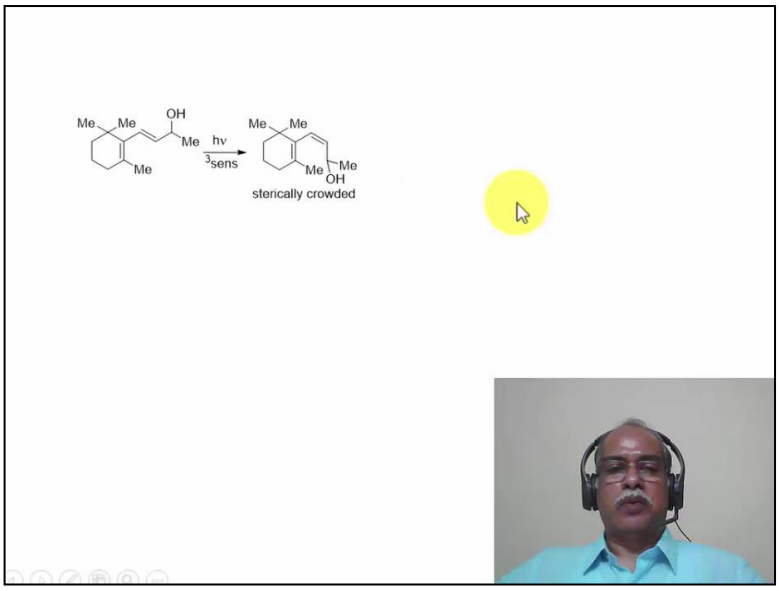

So, it is a very nice way of demonstrating, how Cis-Trans isomerization is very vital in certain processes, that are happening in our body. Now, Cis-Trans isomerization process, is also used in organic synthesis. This is a sterically crowded Cis isomer of the molecule, with a suitable Triplet sensitizer, which will transfer energy only to the Trans isomer. The Trans isomer can be isomerized to the Cis isomer, constituting a synthesis of highly sterically hindered molecule.

This is sterically hindered, because of the two Methyl groups are poking at each other, and the Hydroxy group is also in close proximity to the Methyl group of the ring, for example. Compared to the Trans, where the two Hydroxy and Methyl groups, are away from this particular Methyl group. So, sterically hindered molecules of this type, several Retinal's have been synthesized, using the sensitization process.

This is a unidirectional sensitization process. Because, the Cis isomer is not sensitized, by the Triplet sensitizer. Only, the Trans isomer is sensitized, by this Triplet sensitizer. Because, that only can receive, the energy of the Triplet sensitizer. So, the Trans isomer gets converted into the Cis isomer, exclusively in this particular case.

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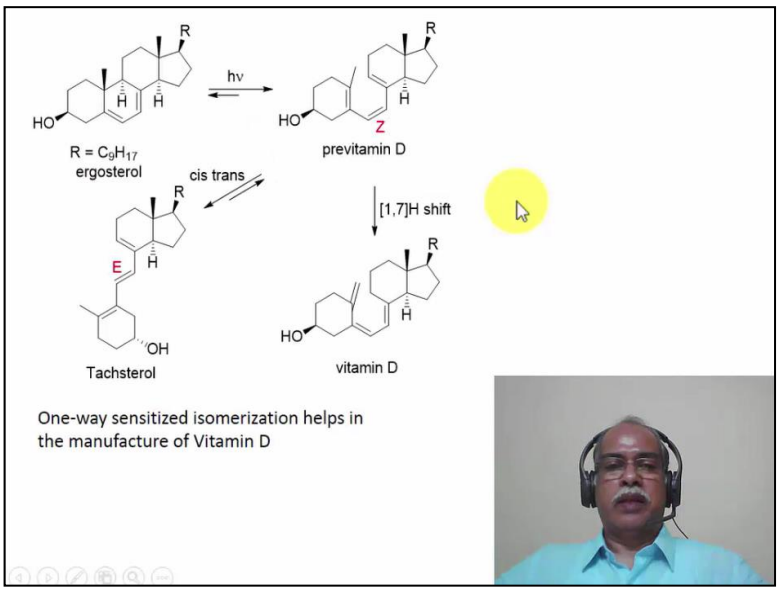

This process of unidirectional sensitization are, one-way sensitization of a molecule is used, in the industrial synthesis of Vitamin-A. This is Vitamin-A. The structure of Vitamin-A, is shown here. The precursor for Vitamin-A is Ergosterol, which has this particular structure. Ergosterol, on photolysis, undergoes Electrocyclic ring opening of this Cyclohexadiene unit, into a Hexatriene unit of this kind, for example.

Now, this process is essentially a Conrotatory process, because of the fact that, it is a 4N+2-Electron system. And, it is undergoing a Photochemical kind of a Electrocyclic ring opening process, that will give the stereochemistry, as it indicated here, with the Z isomer being formed here. Now, Z isomer under the photolytic condition, can also undergo Cis-Trans isomerization. Once, it goes to the Trans isomer, this is a useless molecule. The Tachysterol, is not a precursor for Vitamin-D.

So, one need to use the Previtamin-D selectively, to undergo another [1,7]-Hydrogen shift. The Hydrogen from this Methyl group, is shifted onto the 7-Position. This is 1-2-3-4-5-6-7. So, the Hydrogen is shifted to the 7th position, which is a [1,7]-Sigmatropic shift, Hydrogen shift, resulting in the formation of Vitamin-D. If the Previtamin is partitioned, between the Cis-Trans isomerization, and a Vitamin-D process, then the efficiency will go down.

So, what happens is, this Triplet sensitizer is used, such that the Triplet sensitizer energy, is transferred only to the Tachysterol, which is a Trans isomer, converting exclusively to the Cis

isomer, which is the Previtamin-D. And, the Previtamin-D, now undergoes the thermal [1,7]-Hydrogen shift, to give the Vitamin-D, which is the useful molecule.

So, industrial synthesis of Vitamin-D, essentially proceeds by a Cis-Trans isomerization process, selectively sensitized by a Triplet sensitizer, that sensitizes the conversion of the Tachysterol, to Previtamin-D. This is a thermal process. This has nothing to do, with Photochemistry. This is a Thermal [1,7]-Shift taking place, in an Antarafacial manner, in this particular molecule.

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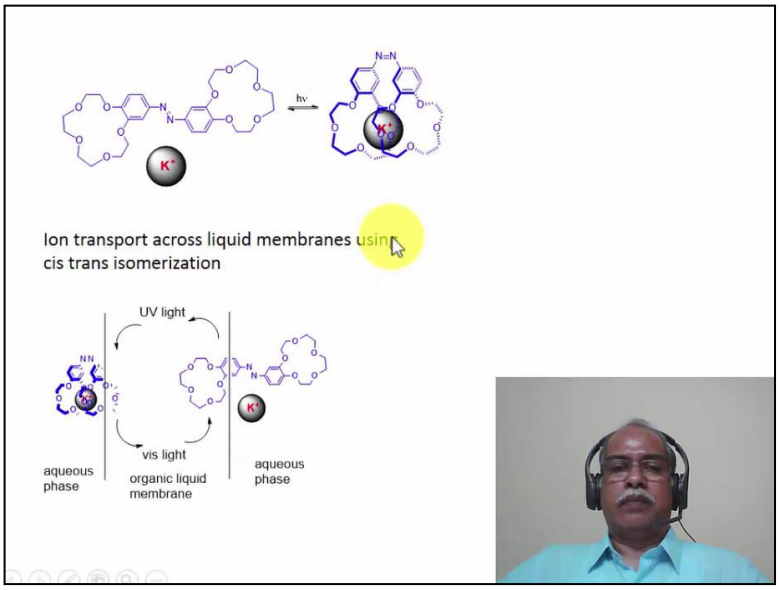

Another utilization of the Cis-Trans isomerization, is to do the Ion transport, across the liquid membranes, using the Cis-Trans isomerization process. This is an Azo molecule. This is an Azo Benzene molecule, which is linked to a Crown Ether, which is a 5-Crown Ether. There are 5-Oxygen atoms, in this. The 5-Crown Ether is not capable of, encapsulating a Potassium Ion, unless it is sandwiched between two, 5-Crowns of this kind, for example.

A single 5-Crown, will not be able to accommodate, Potassium. Because, Potassium is too large to fit, into this cavity. However, it can be nicely sandwiched between this two, crown Ether rings. That is possible, only if it is existing in the Cis configuration. This is a Trans configuration, where the two crown Ethers, are far away from each other. When it undergoes Photochemical isomerization, to the Cis isomer of the Azo Benzene, the two crown Ethers, are now facing each other, encapsulating the Potassium Ion.

Now, imagine, there is Potassium chloride solution, on this side of the cell, which is separated by an organic layer. When the other side, there is Aqueous phase, without any Potassium, let us say for example. Now, the crown Ether is capable of partitioning, both in

the organic layer, as well as in the Aqueous layer. And, when you shine light on it, the Trans isomer, undergoes the Cis-Trans isomerization.

Once, it undergoes Cis-Trans isomerization, it can go to the side, which contains the Potassium Ion. Encapsulate the Potassium Ion, and bring it to the organic layer. And, cut across the organic layer, to come to the other side. And, if it is now excited with visible light, because the Cis isomer absorbs the visible light, and the trans-isomer absorbs the UV light. So, one can selectively do the Cis to Trans, or the Trans to Cis isomerization, using the proper wavelength of light.

So, once it is exposed to the visible light, it will undergo, again Trans isomer. Trans isomer, of course, will release the Potassium Ion, it will not hold it. So, it will release a Potassium Ion. And, on the Aqueous phase, which originally did not contain, any Potassium Ion. So, essentially you are transporting the Potassium Ion, across a liquid membrane, which is an organic solvent, in this particular case. This kind of mechanistic information, can be readily obtained, by the Cis-Trans isomerization studies.

So, what we have seen in this module, is the process of Cis-Trans isomerization of Olefin. The mechanism by which, the Cis-Trans isomerization can proceed. The effect of the Triplet sensitizer energy, on the Cis-Trans isomerization Photostationary state. Several examples of Cis-Trans isomerization, in chemical system, as well as in Biological system. I hope, you enjoyed this particular module. Thank you very much, for your kind attention.