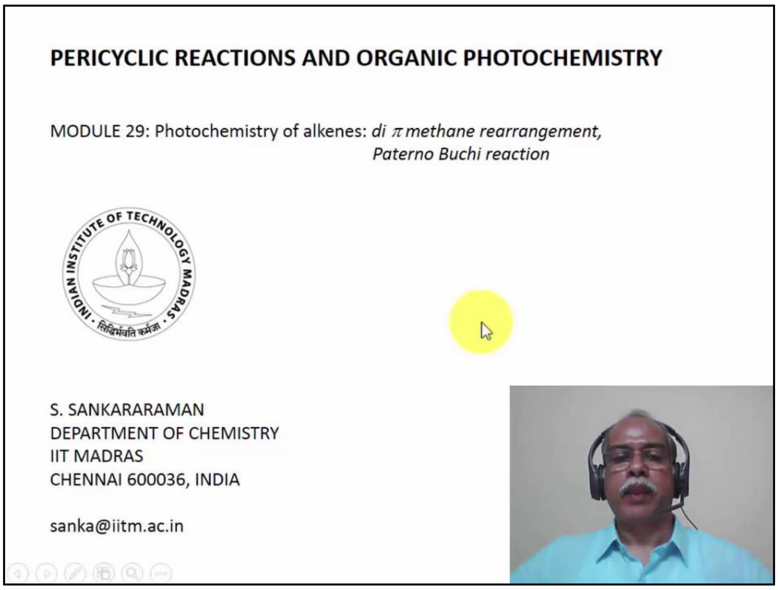
Pericyclic reactions and Organic Photochemistry
S. Sankararaman
Department of Chemistry
IIT Madras, Chennai 600 036, India

Module No. #07
Lecture No. #29
Photochemistry of Alkenes: Di π Methane Re-arrangement, Paterno-Buchi reaction

(Refer Slide Time: 00:11)



PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

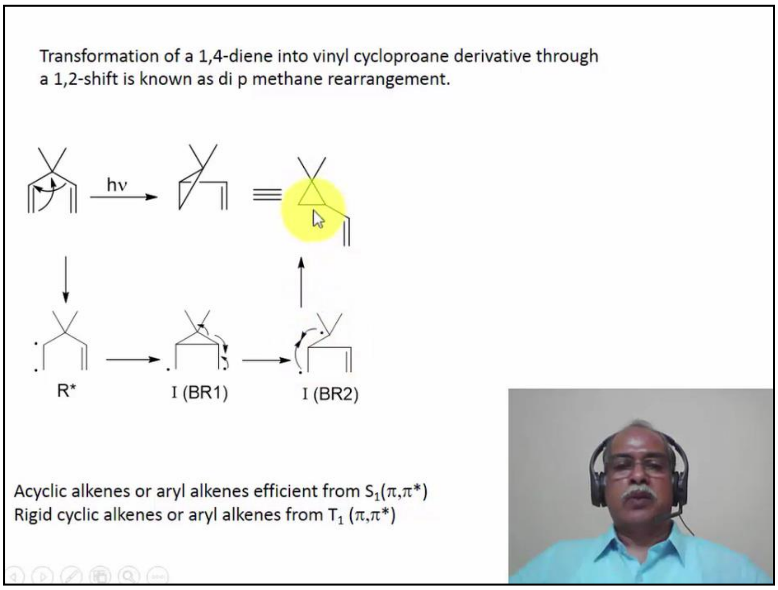
MODULE 29: Photochemistry of alkenes: *di π methane rearrangement,*
Paterno Buchi reaction

S. SANKARARAMAN
DEPARTMENT OF CHEMISTRY
IIT MADRAS
CHENNAI 600036, INDIA

sanka@iitm.ac.in

Hello, welcome to the online course on, Pericyclic Reactions and Organic Photochemistry. This is Module Number Twenty-Nine. We will continue with the, Photochemistry of Alkenes. There are two important reactions, that we need to go through, in this particular module. One is called the Di-PI-Methane rearrangement. The another one is called the Paterno-Buchi reaction. Paterno-Buchi reaction, we will consider little later. First, we will consider, the Di-PI-Methane rearrangement.

(Refer Slide Time: 00:37)



Transformation of a 1,4-diene into vinyl cycloproane derivative through a 1,2-shift is known as di p methane rearrangement.

Acyclic alkenes or aryl alkenes efficient from $S_1(\pi,\pi^*)$
Rigid cyclic alkenes or aryl alkenes from $T_1(\pi,\pi^*)$

Di-PI-Methane rearrangement is a transformation, that is investigated by Zimmerman. So, this rearrangement is, sometime also known as Zimmerman’s reaction. This is a transformation of a 1,4-Diene. If you consider this Diene, this is 1,4-Pentadiene. 1-2-3-4-5. So, this is 1-2-3-4, 1,4-Diene. It is a 1,4-Pentadiene, is what, we have. The 1,4-Pentadiene, under the Photochemical excitation, undergoes a transformation to Vinyl Cyclopropane.

So, this is the Vinyl Cyclopropane, that is formed, by a formal 1,2-Shift, which is known as the Di-PI-Methane rearrangement. This should be PI, not P. Di-PI-Methane rearrangement, is what we have. So, the mechanism simplistic manner, we can show that, this is a migration of a bond to here, forming a 3-Membered ring here, followed by migration of this Carbon-Carbon bond, onto this particular Carbon, for example, resulting in the formation, of a Vinyl Cyclopropane kind of a derivative. The mechanism is more clearly, shown here.

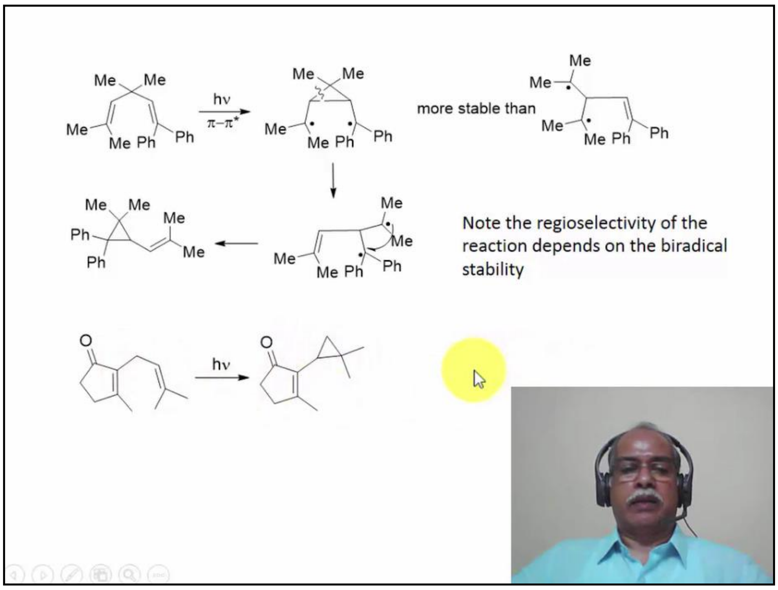
PI to PI-Star excitation, essentially results in the formation of an excited state species, which is a Diradical species. The Diradical species, undergoes the ring closing reaction, because of the proximity of the 1,4-Diene. Having this bulky substituent, in this 3-Position, helps in bringing the interaction, between these two. That is why, Di-PI-Methane rearrangement, is always carried out with, substituent being present here. Whether, Dimethyl substituent, or Diphenyl substituent, as the case may be.

Just to bring the proximity of these two double bonds close to here, for the orbital interaction to take place. So, essentially, once the Diradical state is formed, it undergoes the ring closing reaction, across here, to form another Diradical intermediate. This Diradical intermediate, can now undergo a Cyclopropane bond cleavage, producing another 1,3-Diradical species, and a double bond will be here. The 1,3-Diradical recombines, to form the Cyclopropane.

So, the Cyclopropane ring formation, essentially takes place by the ring closure of a distant 1,3-Diradical, undergoing a Dimerization kind of a process, to give the 3-Membered ring, in this particular case. Turns out that, Acyclic Alkenes and Aryl Alkenes, which are part of the Acyclic Alkenes, undergo this Di-PI-Methane rearrangement very efficiently, from the Singlet excited state, which is a PI to PI-Star state.

Whereas, the rigid Cyclic Alkenes, and Aryl Alkenes, which are part of the Cyclic Alkenes, efficiently undergo this reaction, from the Triplet PI-PI-Star state. Remember, the Triplet PI-PI-Star state can be easily accessed, by a Triplet sensitizer. Direct excitation, invariably give in the case of Alkenes, the Singlet PI to PI-Star excited state. So, when the reaction is carried out, under sensitization condition, one can access the Triplet state, from which the Rigid Cyclic Alkenes undergo efficient reaction, which is the Di-PI-Methane rearrangement.

(Refer Slide Time: 03:32)



Note the regioselectivity of the reaction depends on the biradical stability

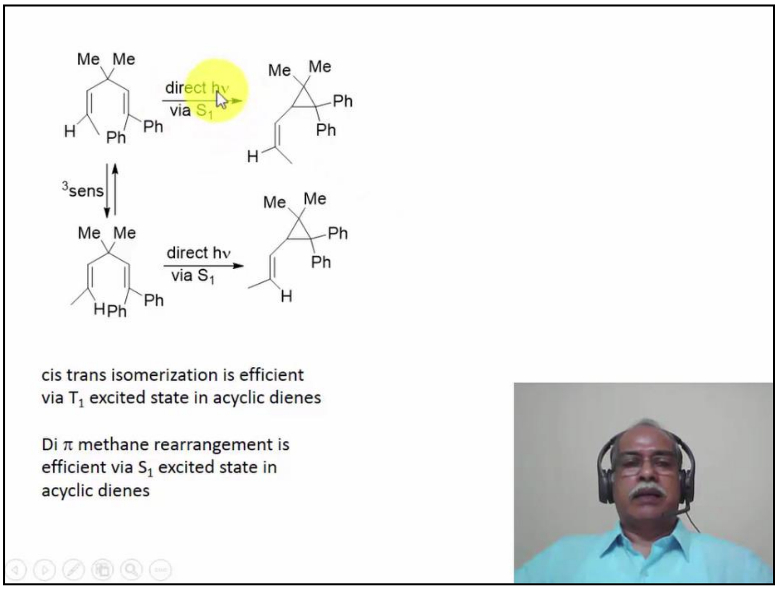
Di-PI-Methane rearrangement of Unsymmetrically substituted derivative. What is Unsymmetrical about this. This double bond is substituted with, Methyl functional group, whereas this double bond is substituted with, Phenyl derivative. Only, one product is formed, which is this particular product. Other possible product could be, where you have Dimethyl group here, and the Diphenyl group here, which is not formed, in this particular reaction. The reason is, once the Diradical is formed, the cleavage of this bond, or this bond, is what takes the reaction, further.

This bond is selectively cleaved, for the reason that, the radical that is produced, is a highly stable radical. This is a Diphenyl Methyl radical. And, this is an Isopropyl kind of a radical, Tertiary-Butyl kind of radical, for example. On the other hand, if you break this Carbon-Carbon bond, which is the other Cyclopropyl bond, you will end up with, the Dimethyl substituted Methyl radical here, similarly, Dimethyl substituted Methyl radical. This radical, does not have the radical center, at the Phenyl substituted Carbon.

So, this will be much less than the radical, which is produced by the Diphenyl Methyl Carbon, which is this particular Carbon. Because of the stability of the radical, that is being intermediate radical, that is being produced being more, in this particular case, the reaction proceeds in a Regioselective manner, to produce this particular product. The other product, where you have Tetramethyl in the Cyclopropyl, and Diphenyl in the Olephinic double bond is not formed, because of the stability of the intermediates, being very strong in this particular case, compared to this case, here.

Here is another example, of a Di-PI-Methane rearrangement, where the one of the double bond is part of an Enone. Enone undergoes, essentially a Di-PI-Methane rearrangement, in a Regioselective manner again, to give a Vinyl Cyclopropane, where the double bond is in still in conjugation with the, Carbonyl functional groups. So, essentially it is the shifting of this particular bond, followed by the shifting of this bond over here, resulting in the formation of the Cyclopropyl derivative.

(Refer Slide Time: 05:31)



cis trans isomerization is efficient via T_1 excited state in acyclic dienes

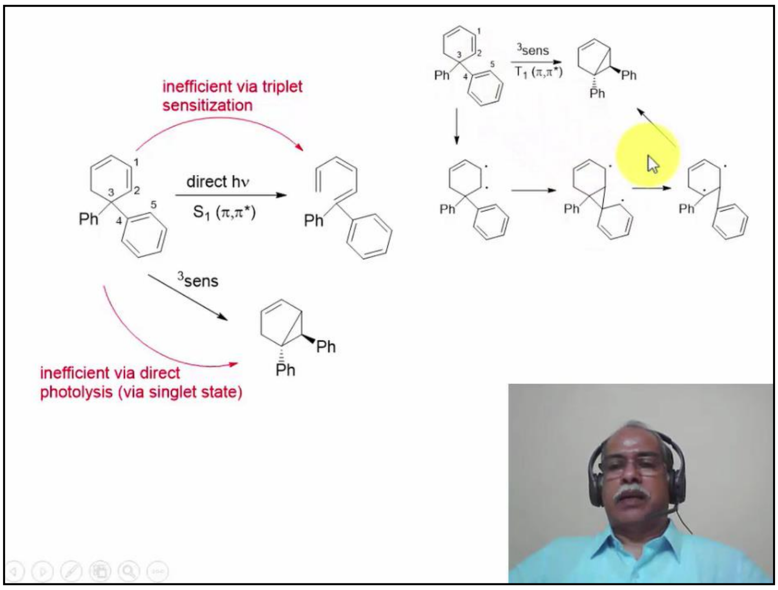
Di π methane rearrangement is efficient via S_1 excited state in acyclic dienes

Now, this is essentially to illustrate the point, that the Acyclic Dienes isomerize under the Singlet state, more efficiently, compare to the Triplet state. If you take this molecule, this is the Z isomer, of this molecule. This is a Cis isomer of the molecule. Under, PI-PI-Star Singlet excited state, because of the direct irradiation, which is absorbed by the double bonds here, essentially there is a Di-PI-Methane rearrangement, that is taking place.

And, there is no Cis Trans isomerization taking place. You can see here, this is still a Cis isomer, that is being formed. On the other hand, if a Triplet sensitizer is used, predominately the Cis Trans isomerization, is what takes place. The Trans isomer also, if you take pure Trans isomer, and do a direct photolysis, the reaction proceeds via Singlet excited state. Under those condition, the Trans double bond remains as a Trans double bond, nevertheless, the molecule has undergone the Di-PI-Methane rearrangement.

Again, because of the Unsymmetrical nature of the molecules, very Regioselective, Di-PI-Methane rearrangement, is what is taking place. So, the Triplet sensitizer can promote, only the Cis Trans isomerization. Whereas, a Singlet state, which is obtained by the direct photolysis of the molecule itself, will promote the Di-PI-Methane rearrangement. Because, this is an Acyclic Diene, of this kind.

(Refer Slide Time: 06:56)



In the case of Cyclic Diene, it is the other way around. It is a Triplet sensitizer, which promotes the Di-PI-Methane rearrangement. We will come to the mechanism of the Di-PI-Methane rearrangement, in a minute. This is, believe it or not, it is a Di-PI-Methane system. We can see here, this is 1,4-Pentadiene, is what we have. Where, Diene portion, is actually part of an aromatic ring system, here. So, the numbering starts from here, 1-2-3-4-5.

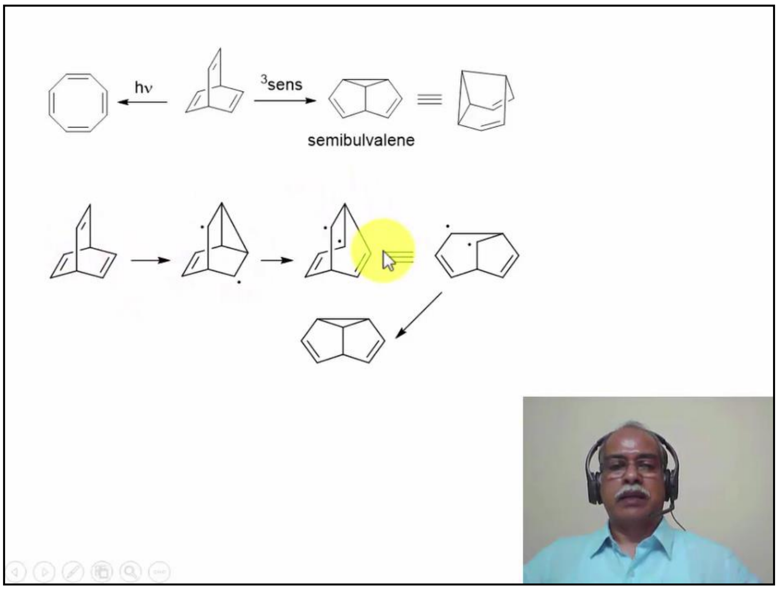
So, this is a Penta-1,4-Diene, is what we have, in this particular system, which undergoes the Di-PI-Methane rearrangement, under the sensitized condition. Because, this is cyclic system, which is undergoing the Di-PI-Methane rearrangement, not an Acyclic system. On the other hand, direct photolysis gives, simple electrocyclic ring opening of this particular bond. Remember, this is also Cyclohexadiene. It can undergo, electrocyclic ring opening reaction, to give the Hexatriene molecule, which is this particular molecule.

So, what is a mechanism of this reaction. To just to complete the story, it is the Singlet state, which is responsible for the electrocyclic ring opening reaction. It is a Triplet PI-PI-Star state, which is responsible for the Di-PI-Methane rearrangement. If we try to do it, the other way, the Triplet sensitized ring opening, is inefficient. Because, under the conditions of the Triplet sensitizer, only this reaction proceeds, this reaction does not proceed.

So, it is inefficient via Triplet state. Whereas, the Di-PI-Methane rearrangement is inefficient, via the Singlet excited state. So, direct photolysis will produce, only this, and not this. Just to emphasize the point, this is given in the Red color. The mechanism of isomerization, is shown here, very clearly. This is the double bond, which is participating in the Di-PI-Methane rearrangement. A Diradical is initially produced of the Olefin. Then, the ring closing reaction takes place, producing a 1,5-Diradical of this process.

Then, the Cyclopropyl bond, undergoes the cleavage, to produce the aromatic compound back. The Phenyl ring is regenerated, resulting in the formation of a 1,3-Diradical. 1,3-Diradical, undergoes the ring closing reaction, to give the Cyclopropyl derivatives. So, you get the Vinyl Cyclopropane, which is a Di-PI-Methane rearranged product. So, the part of the Di-PI-Methane system, is the aromatic system itself, in this particular instance. It temporarily loses its aromaticity, and regains its aromaticity, during the course of the Di-PI methane.

(Refer Slide Time: 09:25)



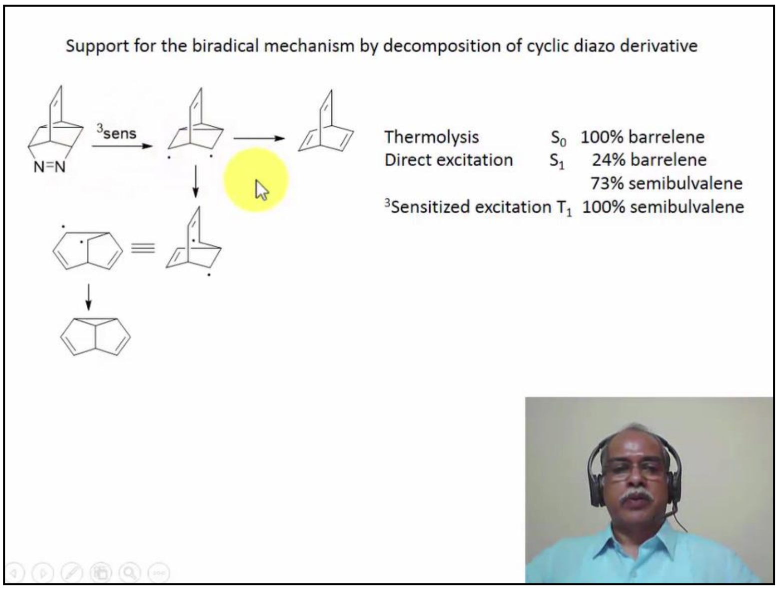
This molecule, is known as Barrelene. Because, it is supposed to look like a barrel. It is actually a Di-PI-Methane system, if you look at this Pentadiene, or this Pentadiene, or this Pentadiene. So, it is a threefold axis of Symmetry, is there. And, this PI bonds, essentially serve as the Di-PI-Methane system. Under the photo sensitized condition, it undergoes the photo isomerization, to give Semibullvalene. So, when a sensitizer is used, it undergoes the, this is a constrained Cyclic Diene, that is why, it undergoes a Triplet sensitized Di-PI-Methane rearrangement.

This molecule, essentially has this particular shape, which is the Cyclopropyl, with the boat kind of a 7-Membered ring here, connected by the bridge, which is this particular bridge, here. The mechanism is shown here. Initially, PI-PI-Star excitation, produces a Diradical here, which undergoes the ring closing, to give the Cyclopropyl derivative, with the 1,5-Diradical. The 1,5-Diradical, the Cyclopropyl ring is opened again, resulting in the formation of the double bond here, and a 1,3-Diradical.

This molecule, you should be able to visualize, same as this particular molecule. You can imagine here, there is a bridging radical here, which is this bridging radical here, essentially you have a 1-2-3-4-5-6, 7-Membered ring, with a bridging radical. So, you start from here, it is a 7-Membered ring, with the bridging radical. This is a 1,3-Diradical.

This undergoes a ring closing, to give the Cyclopropyl ring system. So, exactly the same mechanism as earlier, shown for the Di-PI-Methane rearrangement, except it is in a sort of a constraint Cyclic system, undergoing the ring closing reaction. Under direct photolysis, under Singlet PI to PI-Star excitation, Barrelene essentially undergoes isomerization, to give the Cyclooctatetraene, as the product.

(Refer Slide Time: 11:11)



Support for the biradical mechanism by decomposition of cyclic diazo derivative

Thermolysis	S_0	100% barrelene
Direct excitation	S_1	24% barrelene 73% semibulvalene
^{3}Sensitized excitation	T_1	100% semibulvalene

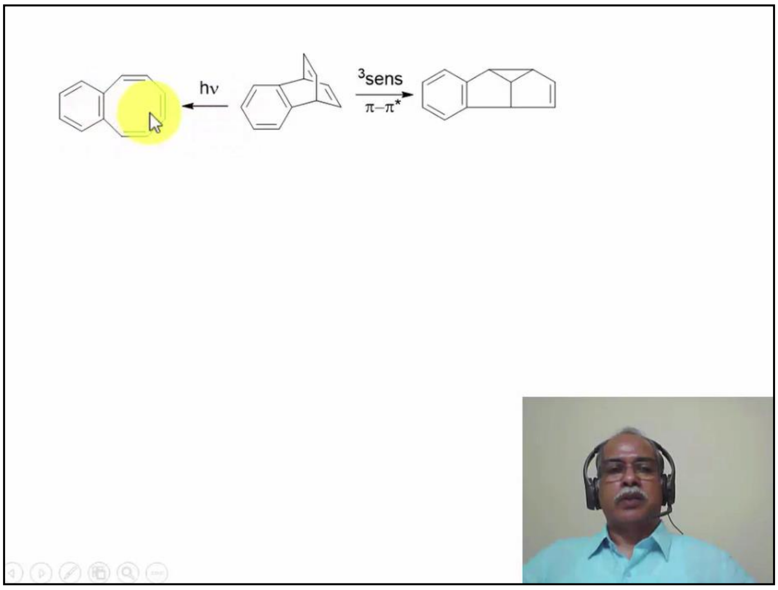
Now, the proof for the Diradical mechanism, essentially comes from this experiment. If you take this cyclic Diazo compound, under sensitized condition, one photolysis the molecule, this Diradical is produced. Remember, this is the same Diradical, which is this particular Diradical, in the mechanism.

And, this essentially produces the Barrelene, by cleavage of the Cyclopropyl bond, to give these two double bonds, by the radical recombination here. Or, it can undergo the cleavage of this particular Carbon-Carbon bond of the Cyclopropyl system, to give this Diradical, which is the 1,3-Diradical, same Diradical, that is produced, in the case of the Barrelene photolysis also. So, the detection of the mechanism that, this Diazo compound can decompose, to give Nitrogen, and this Diradical.

And, this Diradical can produce a Semibullvalene, which is also obtained from the direct photolysis, sensitized photolysis of this molecule, to give the Barrelene, clearly shows that, this is a mechanism, which is a proof for the Diradical intermediate. So, thermolysis of the molecule, which produces in the ground state, 100% Barrelene is produced. Essentially, it probably is not going through a Diradical mechanism, under the thermolysis condition. It depends on the temperature, we do not know the condition.

It produces only Barrelene. Direct excitation, produces Barrelene, as well as Bullvalene, in the Semibullvalene, extent of about 24% and 73%, respectively. Whereas, a Triplet sensitized photo isomerization, essentially loss of the Nitrogen, produces, 100% of the Semibullvalene. So, this is taken as a mechanistic proof, for the formation of the Diradical, and subsequent rearrangement of the Diradical, to form the Semibullvalene, which is the photo isomerized product of the Diazo compound.

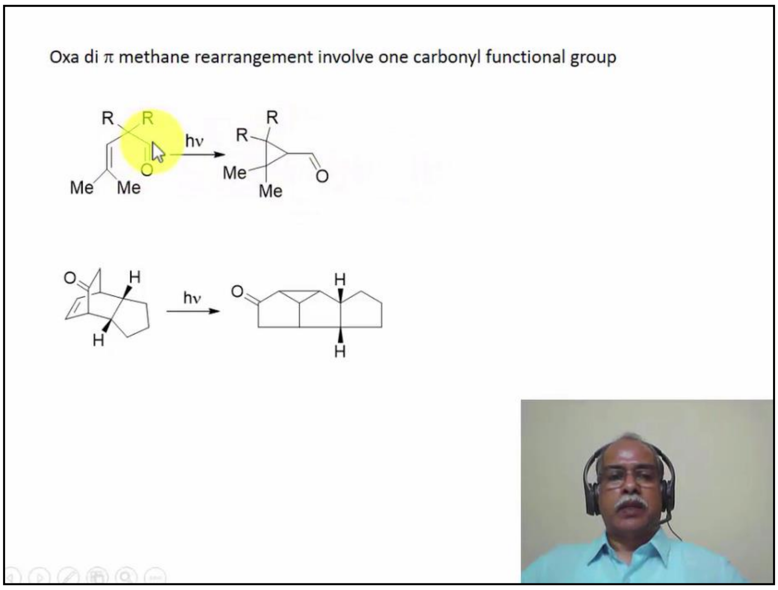
(Refer Slide Time: 13:00)



This is another example of the Benzo Barrelene. Benzo Barrelene, undergoes Triplet sensitized PI-PI-Star excitation, resulting in the formation of Di-PI-Methane rearrangement. The Di-PI-Methane rearrangement system, is shown here, very clearly. And, it produces a

Vinyl Cyclopropane as the derivative, that is formed. Direct photolysis produces, Benz Cyclooctatetraene as the product, in this particular case.

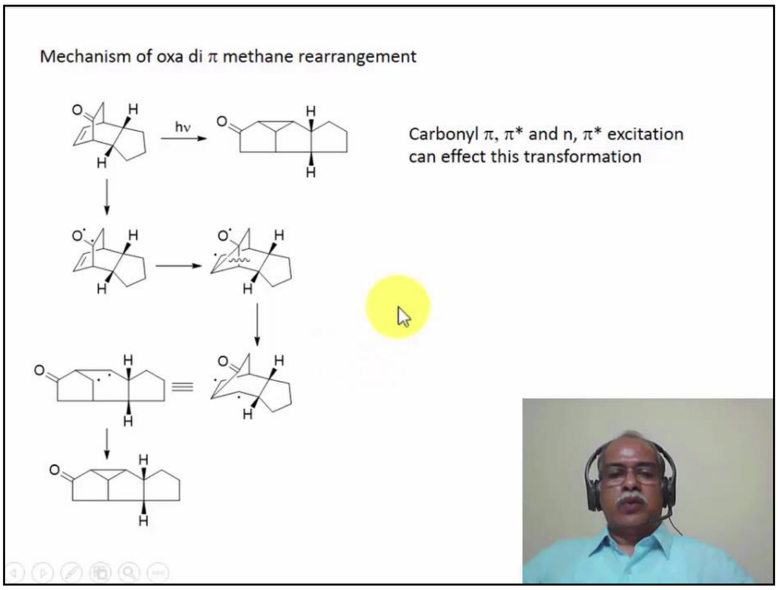
(Refer Slide Time: 13:24)



Oxa di π methane rearrangement involve one carbonyl functional group

The Carbonyl bond can be part of the, Di-PI-Methane rearrangement system, in which case, it is called Oxa-Di-PI-Methane rearrangement. Oxa-Di-PI-Methane rearrangement involves, one Carbonyl functional group, and one double bond, in this particular case. The reaction is highly Regioselective, in the sense that, it produces only a Cyclopropyl Aldehyde, in this particular case. Here is another example of an Oxa-Di-PI-Methane rearrangement, producing this particular molecule.

(Refer Slide Time: 13:54)



Mechanism of oxa di π methane rearrangement

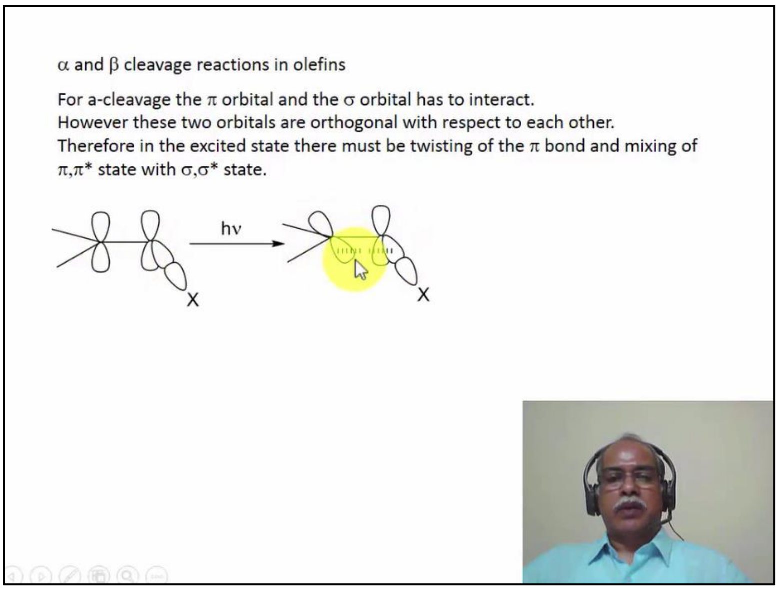
Carbonyl π, π* and n, π* excitation can effect this transformation

The mechanism of it is, very clearly shown here. Initially, either the PI-PI-Star excitation of the Carbonyl, or the N-PI-Star excitation of Carbonyl, can effect this particular transformation. The Oxa-Di-PI-Methane rearrangement, proceeds by the excitation of the, either the PI-PI-Star, or the N-PI-Star state of the Carbonyl functional group, to produce this excited state, which is considered to be a Diradical kind of an excited state.

The Diradical excited state, undergoes the ring closing, to give the Cyclopropyl ring closed product, which is this product, gives the 1,5-Diradical, in this particular case. The 1,5-Diradical, undergoes the cleavage of the Cyclopropyl bond, regenerating the Carbonyl functional group, and a 1,3-Diradical. The 1,3-Diradical, is this particular structure.

It undergoes recombination, to give the 3-Membered ring. And, that is the same product, that is given in the scheme, that is shown here. So, this is a mechanism, involving a 1,5-Diradical, and a 1,3-Diradical, and so on, which was investigated by Zimmerman, to propose. This is called the Zimmerman mechanism, of the Di-PI-Methane rearrangement.

(Refer Slide Time: 15:00)



α and β cleavage reactions in olefins

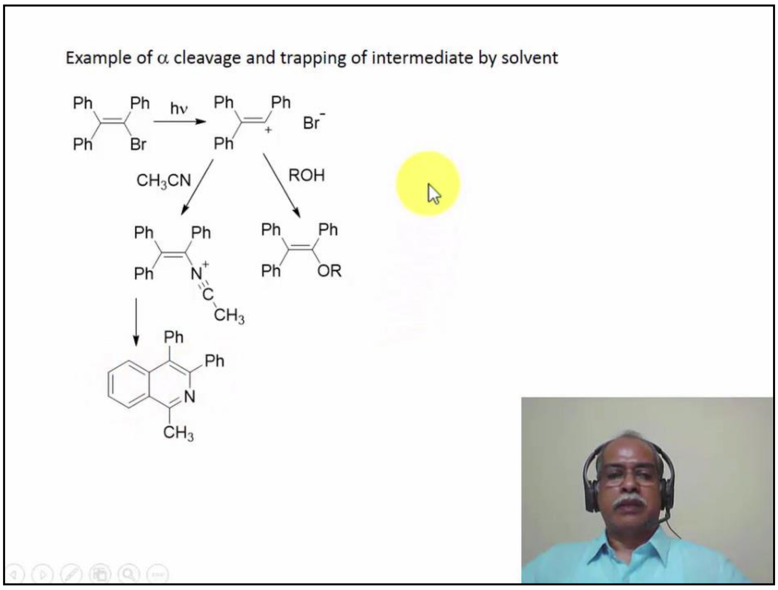
For a-cleavage the π orbital and the σ orbital has to interact.
However these two orbitals are orthogonal with respect to each other.
Therefore in the excited state there must be twisting of the π bond and mixing of π,π* state with σ,σ* state.

Now, Olefins can also undergo Alpha cleavage, or the Beta cleavage, that is from the Olefinic bond, either the Alpha bond, which is this Carbon X bond, or a Beta bond, which we will show little later, for example. These are the two processes, that can take place. Now, let us first consider, the Alpha cleavage. This is not A cleavage. This is Alpha cleavage. This should be Alpha. The Alpha cleavage essentially, involves two orbitals.

The excitation corresponds to the, PI-PI-Star excitation, however the CX bond, is what is breaking. The CX bond is actually, Orthogonal to the PI molecular orbital of the double bond. So, Orthogonal orbitals, do not interact, with each other. So, how do we transfer the energy, that is exciting this PI bond, onto this bond, so that, this bond can be cleaved. It has to attain, some kind of a twisted geometry, at the excited state.

In the twisted geometry, there can be a mixing of the PI bond and the Sigma bond, which is indicated by this dash line. So, in this case, it is Orthogonal. But, in this case, it is not Orthogonal, because of the twist. There is a participation of this P-Orbital on to the Sigma bond, Sigma star orbital of this particular CX bond, which will result in the ionization of this molecule.

(Refer Slide Time: 16:18)

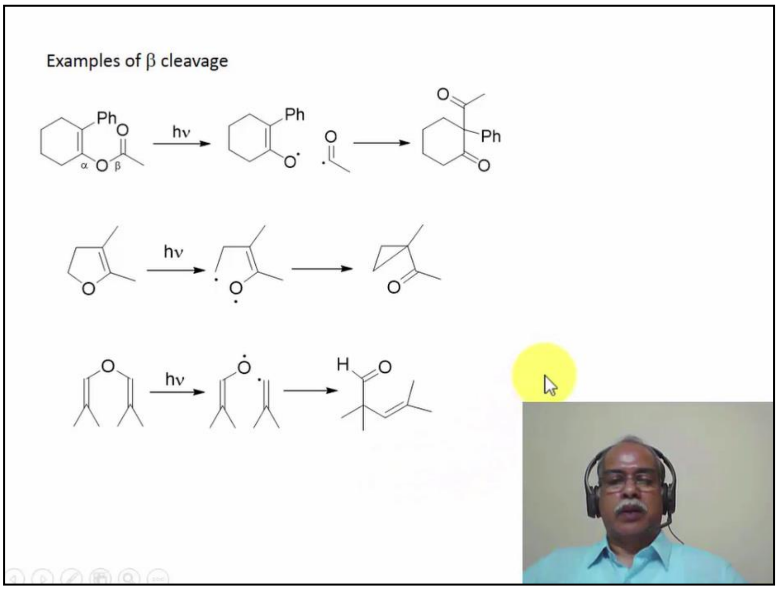


Example of α cleavage and trapping of intermediate by solvent

One example of the Alpha cleavage, is shown here. This is Triphenyl substituted Vinyl Bromide. It under Photochemical condition, the CBR bond is broken, because of the PI-PI-Star excitation, which transfers energy on to the Sigma star orbital of this molecule, resulting in the formation of the ionization, Bromide ion is produced, and this Carbonium Vinyl Carbonium ion is produced. This can be trapped by the alcohol, to produce the corresponding Vinyl Ether. Or, it can be trapped. This is a nucleophilic trapping, by the Oxygen lone pair, is what is taking place.

If Acetonitrile is used as a solvent, the Nitrogen lone pair on the Cyano functional group, can trap the intermediate cation, to produce this intermediate. This intermediate, can undergo electrophilic substitution, on this Cis Phenyl group, resulting in the formation of Isoquinoline molecule, which is this particular derivative, which is finally formed in this reaction. This is one example.

(Refer Slide Time: 17:14)

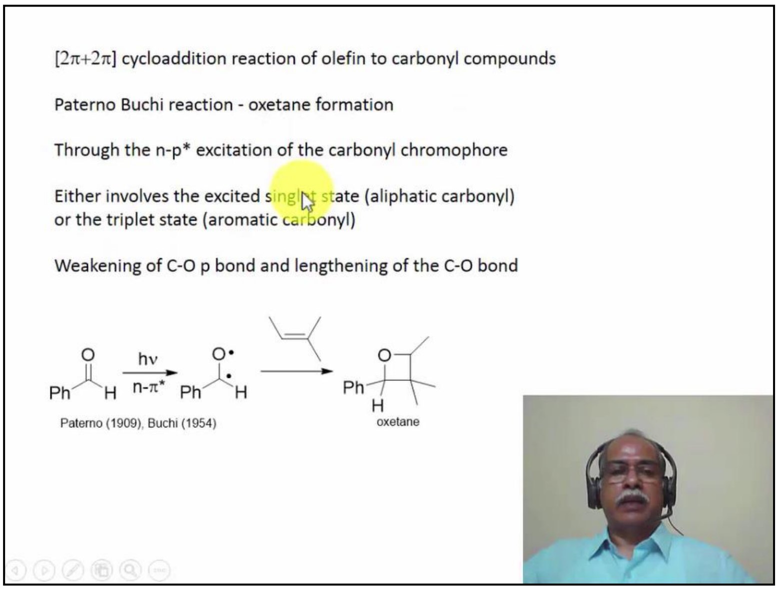

Examples of β cleavage

Let us see the Beta cleavage. Now, this is the PI bond, which is undergoing the PI-PI-Star excitation. This is Alpha bond, with respect to the PI bond. And, this is a Beta bond, with respect to the PI bond. Now, upon direct photolysis, PI-PI-Star molecular orbital is excited. And, that is transferred on to the Sigma orbital of the C Oxygen bond, in this particular case, resulting in the formation of a Diradical. This Diradical, is essentially a Carbonyl Alpha Diradical. You can write the structure, as a radical center here, and the Carbonyl double bond here.

The recombination at this position, essentially produces the Alpha Acyl Cyclohexanone, in this particular case. This is another example, where a Dihydrofuran derivative, is undergoing the Beta cleavage. So, this is Alpha bond, and this is the Beta bond, Carbon Oxygen bond. The Carbon Oxygen bond cleavage, results in the formation of this Enol radical kind of a thing, for example. The Enol radical, is essentially undergoing a recombination here, with a Carbonyl bond being generated, resulting in the formation of a Cyclopropyl Methyl Ketone.

Cyclopropyl Methyl Ketone is the product, that is formed, in this particular case. This looks like a Di-PI-Methane system, but it is not. Because, this Oxygen lone pairs, play alone in this reaction. The PI-PI-Star excitation, essentially produces the Beta cleavage, with this particular cleavage, resulting in the formation of a Diradical recombination at this center, essentially produces this Beta Gamma Unsaturated Carbonyl compound, as the final molecule. So, these are all examples of the, Beta cleavage of the molecule.

(Refer Slide Time: 18:52)



[2π+2π] cycloaddition reaction of olefin to carbonyl compounds

Paterno Buchi reaction - oxetane formation

Through the n-p* excitation of the carbonyl chromophore

Either involves the excited singlet state (aliphatic carbonyl)
or the triplet state (aromatic carbonyl)

Weakening of C-O p bond and lengthening of the C-O bond

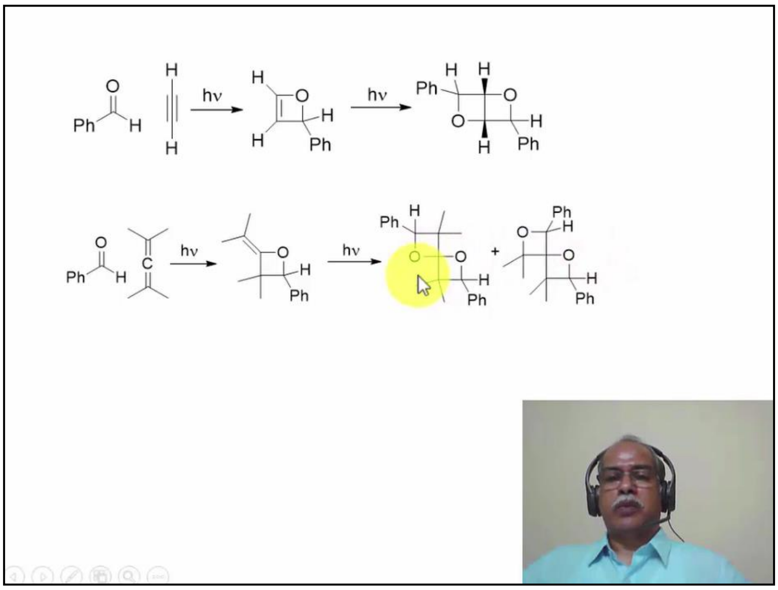
Now, let us go on to, the important 2+2-Cycloaddition reaction. These 2+2-Cycloaddition reaction, is not a concerted reaction. That is why, we are considering it under Photochemistry, not under Pericyclic reaction. The 2PI-2PI Cycloaddition of the Olefin to Carbonyl, to form an Oxetane molecule, is called Paterno-Buchi reaction. Oxetanes are 4-Membered Oxygen Heterocycle, which is shown here.

Now, this reaction can proceed through an, N to PI-Star excitation. This P, is not P, actually it is PI. N to PI-Star excitation of the Carbonyl chromophore, is what is involved in the Paterno-Buchi reaction. It either involves, a Singlet excited state of the Carbonyl functional group, or the Triplet excited state of the Carbonyl functional group, depending upon, we are dealing with Aliphatic Carbonyl, or Aromatic Carbonyl. Because, Aromatic Carbonyl functional group, has a good inter system crossing.

So, the reactions can proceed through, the Triplet state. Whereas, Aliphatic ones, do not have such efficient inter system crossing. So, they will go through a Singlet excited state, of the N-PI-Star state. In the N-PI-Star state, there is a weakening of the PI bond, and lengthening of the CO bond, resulting in the formation of this. So, this is a PI bond, not a P bond. The lengthening of the PI bond of the CO bond, essentially makes it reactive.

It undergoes, a 2PI-2PI Cycloaddition reaction, a formal 2PI-2PI Cycloaddition reaction. The reaction was discovered by Paterno, in 1900. But, until 1954, the structure of the Oxetane, was not established. So, the structure recitation credit, goes to Buchi. The discovery of the reaction, actually goes to Paterno. So, that is why, it is called Paterno-Buchi reaction.

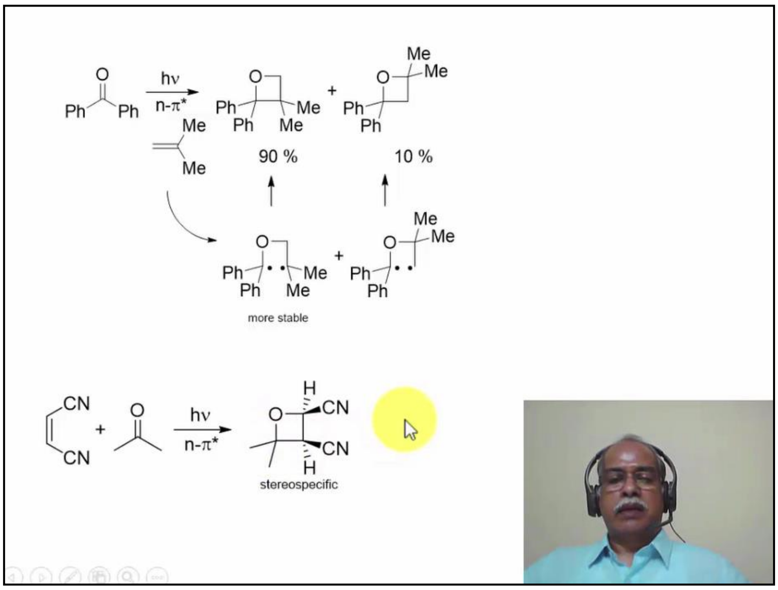
(Refer Slide Time: 20:35)



Now, Paterno-Buchi reaction, is not restricted only to Olefin, the Acetylenes undergo reaction, to give a Cyclo-Oxetane. Oxetane is an extremely reactive Olefin, this will further undergo Cycloaddition reaction, with another molecule of the Carbonyl functional group, to produce Fused Bis Oxetane, which is this particular molecule. In the case of Allene, as an example, again two Cycloaddition reactions are possible, once with this double bond, and once with this double bond.

The first Cycloaddition, produces the Exomethylene Oxetane, as the product. The Exomethylene Oxetane, can undergo Cycloaddition, with another molecule of Benzaldehyde, in two different manner, producing the Regio isomers of the Bis Oxetane, which is a Spiro Bis Oxetane, in this particular case. This is a fused Bis Oxetane, and this is the Spiro Bis Oxetane. There are two isomers possible. Both the isomers, are formed in this reaction.

(Refer Slide Time: 21:29)

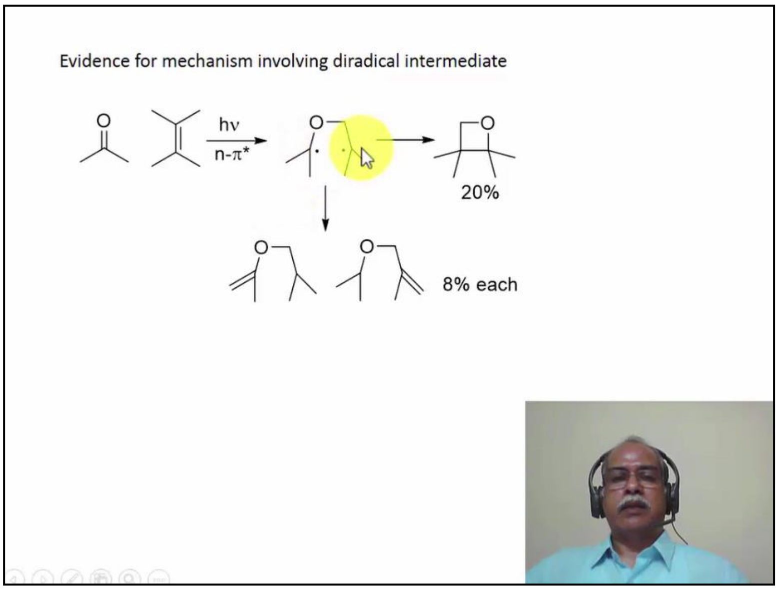


What is the mechanism of the reaction, that is shown, in this particular case. If you take for example, an Unsymmetrical Olefin of this kind, where one Carbon is substituted with the Gem-Dimethyl group, the other Carbon is not substituted at all. Predominantly, this particular product is formed, where this is a highly sterically hindered product, but, nevertheless, that is a major product. The reason being, that the Diradical intermediate, that is formed, is a stable Diradical intermediate.

Whereas, the other Regio isomer, which is this Regio isomer, the Diradical intermediate, that is formed, is this particular intermediate. This is not, as stable intermediate, as this one. So, this is produced in a minor amount, whereas the major amount of the molecule is produced, from the Diradical, that is shown here. In the case of Olefins, with electron withdrawing substituent, such as in the Dicyanoethylene, which is a Cis Dicyanoethylene, the reaction proceeds the N-PI-Star excitation, nevertheless, this reaction is highly stereospecific.

The Cis isomer produces, only the Cis isomer of the Oxetane. This is, in other words, the Dicyano substituted Oxetane, the two Cyano groups, are all in Cis relationship, with respect to each other, just like in the starting material. Although, the reaction proceeds through a Diradical intermediate, the isomerization from Cis to Trans, does not take place, probably because, the Diradical quenching is a much faster reaction, than a Carbon-Carbon bond rotation process, in this particular case.

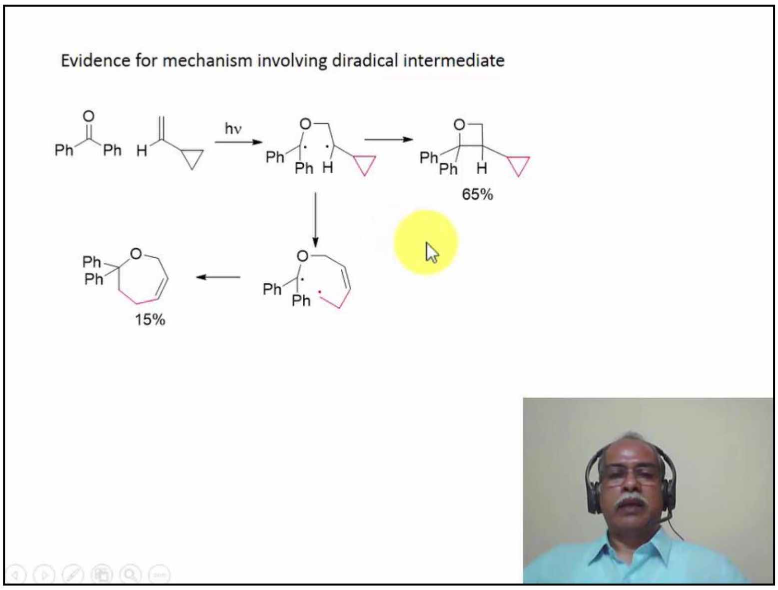
(Refer Slide Time: 22:52)


Evidence for mechanism involving diradical intermediate

Evidence for the Diradical intermediate, comes from these experiments. If you take Tetramethyl Ethylene as the starting material, the Diradical that is produced, can go to the Oxetane, or the Diradical that is produced, can also transfer a Hydrogen from this Diradical, to this particular radical center, resulting in the formation of a double bond here, and a saturated Carbon here. So, you can see here, the Hydrogen has been migrated, from here to this.

Hydrogen atom migration, from here to here, resulting in the formation of 1,2-Diradical, will produce a double bond here, and a saturated Carbon here. Alternatively, the Hydrogen from this Methyl group, can transfer onto this radical center, a Hydrogen atom transfer, resulting in the formation of a double bond. So, the fact that, this Vinyl Ethers are formed, as byproducts in this case, it is an indication that, it could have formed, through the Diradical intermediate.

(Refer Slide Time: 23:46)

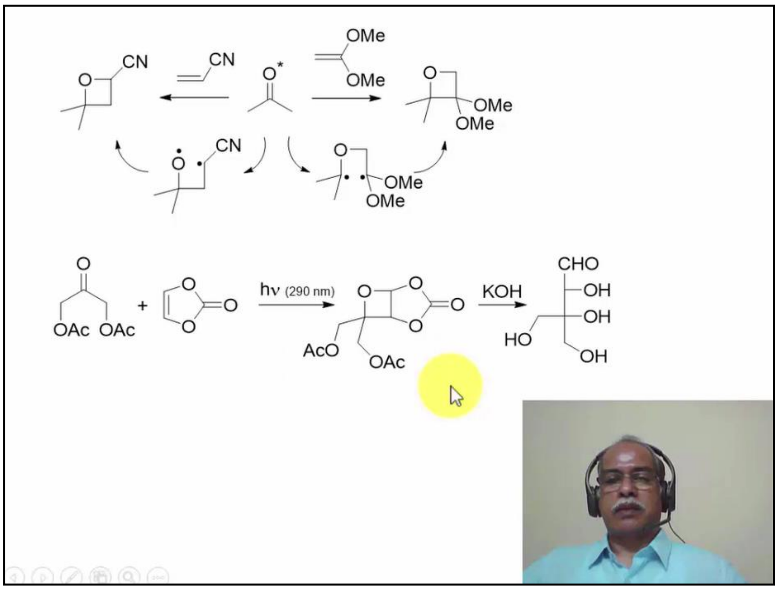


Evidence for mechanism involving diradical intermediate

A more convincing evidence, come from the Cyclopropyl Ethylene, as the substrate in this Paterno-Buchi reaction. When Cyclopropyl Ethylene, is reacted with Benzophenone as the Ketonic component, the Diradical that is generated, has this particular structure. And, this is a Cyclopropyl Methyl radical. Cyclopropyl Methyl radical, have the propensity to undergo ring opening reaction, to give the Butynyl radical, which is this particular radical. The Cyclopropyl part, is given in Red.

So that, you recognize, the three Carbon unit, in all the structures, coming from the Cyclopropyl unit. It can undergo recombination, to give the Oxetane, which is formed in 65% yield. The minor amount of the product, which is this particular product, which is a 7-Membered Oxygen Heterocyclic product, arising from the ring opening of the Cyclopropyl Methyl radical, to the Butynyl radical, which is this particular radical, resulting in the formation of a 7-Membered ring, is taken as a mechanistic evidence, for the Diradical intermediate formation, during the Paterno-Buchi reaction.

(Refer Slide Time: 24:49)



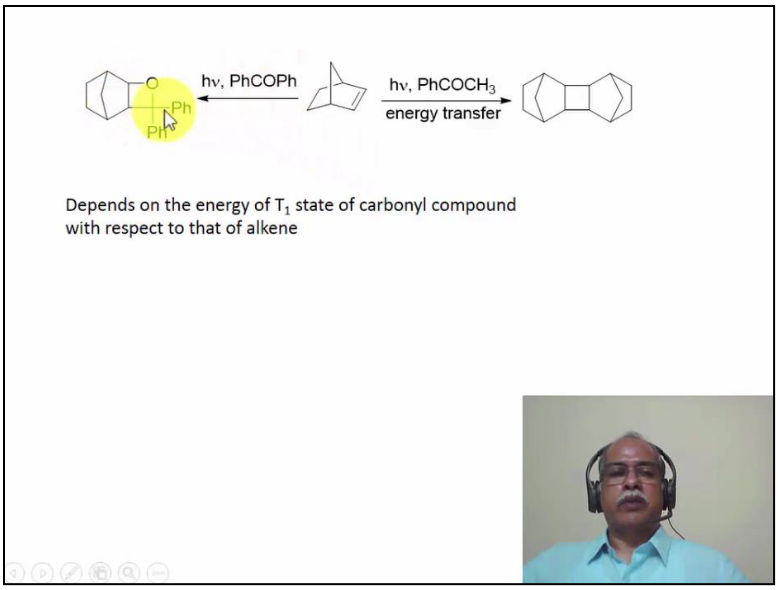
Here again, the Paterno-Buchi reaction, are highly Regioselective, depending upon, whether you have an electron withdrawing functional group, or an electron donating functional group, in the Olefin. The electron withdrawing functional group Olefin, the Dimethyl group of the Ketone, and the Cyano, are in a 1,3-Relationship. Whereas, the Dimethoxy and the Oxygen are again, 1,3-relationship, in this particular case.

Regio chemically, the reaction is explained on the basis that, this is a 1,4-Diradical, that is produced, in the case of the electron withdrawing substituted derivative. This is a more stable radical, compared to the other radical, by forming this bond here, and, producing this two radical, that would be an unstable radical. On the other hand, with the electron donating substituted Olefin, this is the most stable Diradical, that can be formed.

And, hence the Regio isomers are explained, on the basis of the stable Diradical, that can be produced, during the course of the Paterno-Buchi reaction. Here is an example of a Paterno-Buchi reaction of the Ketone, which is shown here, with a Carbonate, which is Acetylene Carbonate, actually.

Under the Photochemical condition, direct photolysis essentially results in the formation of a 4-Membered ring, which is Oxetane. Under the conditions of Alkaline hydrolysis, it essentially produces sugar molecules, because of the presence of the Oxygen functionalities, in this particular system.

(Refer Slide Time: 26:13)



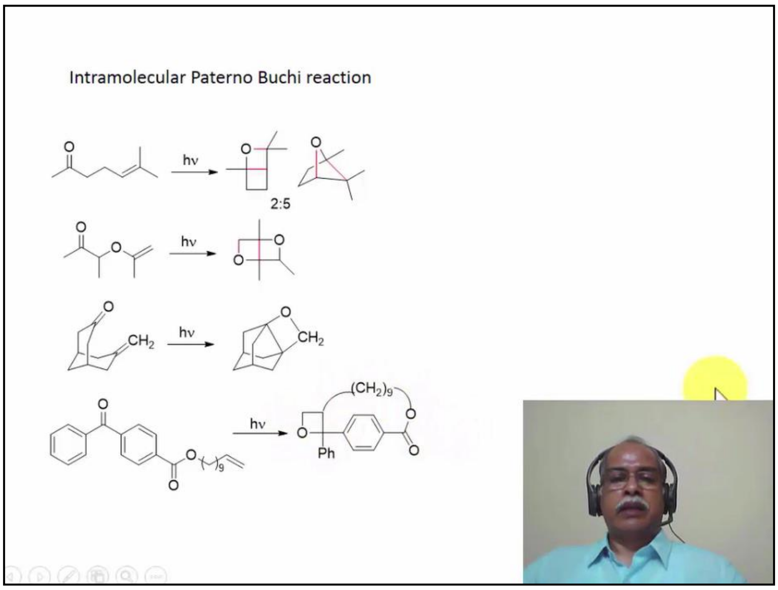
Depends on the energy of T_1 state of carbonyl compound with respect to that of alkene

Now, whether the molecule will undergo, Oxetane formation or not, depends on the Triplet energy of the Carbonyl functional group. In the Triplet energy of the Acetophenone, for example, is higher than the Triplet energy of the Norbornene. Whereas, the Triplet energy of the Benzophenone, is lower than the Triplet energy, or equal to the Triplet energy, of the Norbornene. So, when Acetophenone is used, because the Acetophenone Triplet energy, is at a much higher state, compared to the Norbornene Triplet state.

Energy transfer takes place, producing the excited state of the Norbornene. Once the excited state of Norbornene is formed, the quenching of the excited state of the Acetophenone will take place. From the excited state of Norbornene, it undergoes 2+2-Cycloaddition reaction with itself, producing the Bis Norbornene, which is the 2+2-Cycloaddition process, which would be a concerted process, going through a Triplet kind of a transition state, is what it will undergo, not intermediate stage.

Because, it would be a concerted process. On the other hand, with the acid Benzophenone as the Triplet sensitizer, a 2+2-Cycloaddition reaction, corresponding to the formation of the Oxetane, that is shown here, is what takes place. So, depends on the Triplet energy state of the Carbonyl functional group, with respect to that of the Alkene, one can either form the Alkene 2+2-Addition, or the Alkene Carbonyl 2+2-Addition, which is a Paterno-Buchi reaction. So, these examples, essentially illustrate that particular point.

(Refer Slide Time: 27:44)



Intramolecular Paterno Buchi reaction

Intramolecular Paterno-Buchi reaction examples, are shown here. You can see here, that Red bonds, are the newly formed bonds, in the case of the Oxetane formation. So, there are two ways, one can form the Oxetane, with respect to this, depending upon, how the Carbonyl is oriented, with respect to the double bond. In this particular case, the Methyl group, and the Dimethyl are 1-3, in relationship. So, the orientation is, this is a Carbonyl orientation. This is the Olefin orientation.

In this particular case, the Methyl group, and the Gem-Dimethyl group, are in 1,2-Position. So, this is a Carbonyl orientation, and this is a Methyl Olefin orientation, sort of a criss-cross orientation, is what is given, in this particular case. Here is an example of Alpha Keto Ether, Vinyl Ether, undergoing a Paterno-Buchi reaction, Intramolecular Paterno-Buchi reaction.

All of them are done, using direct excitation, via Singlet excitation PI to PI-Star excitation, resulting in the formation of the fused Bis Oxetane of this kind, where the Red bonds, are the newly formed bonds. So, this should have the Carbonyl functional group, originally. This should have been the double bond, forming these two Red bonds, during the course of the Cycloaddition reaction.

Here, this is a nice geometry, bringing this Carbon functional group, and the Methylene functional group, in close proximity, because of the Axial substituted Ketone, of this kind. So, in this particular conformation, which is the chair conformation, for this particular Ketone, it will bring this Carbonyl functional group, close proximity to the Exomethylene, resulting in the formation of the Oxetane, which is a highly polycyclic kind of a system, is what we have, in this particular case.

Here is a molecule, which is tailor made, to undergo Intramolecular Paterno-Buchi reaction. This Carbonyl, which is the Benzophenone Carbonyl, will undergo the Triplet excitation initially. And, the chain length of this molecule is sufficient, such that, it will undergo the 2+2-Cycloaddition reaction, to form the Paracyclophane derivative, of this kind. So, originally this was the Carbonyl functional group, and this tether group is the Vinylic group.

So, this molecule under very high dilution condition, the unimolecular 2+2-Cycloaddition reaction, essentially produces this Paracyclophane unit, that is shown here. So, what we have seen, in this particular module, there are two types of reaction, that we have seen. Both are very important reactions in Photochemistry, from the mechanistic point of view, as well as from, some synthetic aspect point of view.

One is the Di-PI-Methane rearrangement, of Penta-1,4-Diene molecule. And, it produces the Vinyl Cyclopropane, as the product. The other one is a 2+2-Cycloaddition reaction. It is not a concerted 2+2-Cycloaddition reaction. It proceeds through a Diradical intermediate. And, the Regioselectivities, and the Positional selectivities, can be explained, by means of the Diradical stability. It is known as the Paterno-Buchi reaction. Thank you very much, for your kind attention.