Pericyclic Reactions and Organic Photochemistry
S. Sankararaman
Department of Chemistry
Indian Institute of Technology, Madras

Module No. #07
Lecture No. #31
Photochemistry of Carbonyl compounds: Enone and Dienone Photochemistry

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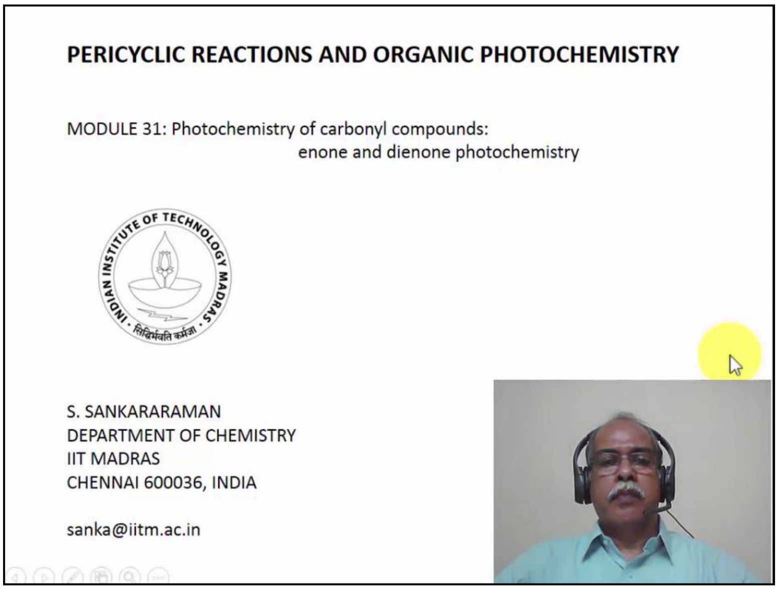

PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY

MODULE 31: Photochemistry of carbonyl compounds:
enone and dienone photochemistry

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. We are in Module Thirty-One, now. In this module, we will consider the Photochemistry of Carbonyl compound, especially the Photochemistry of Enones, and Dienones, in the Organic Chemistry portion.

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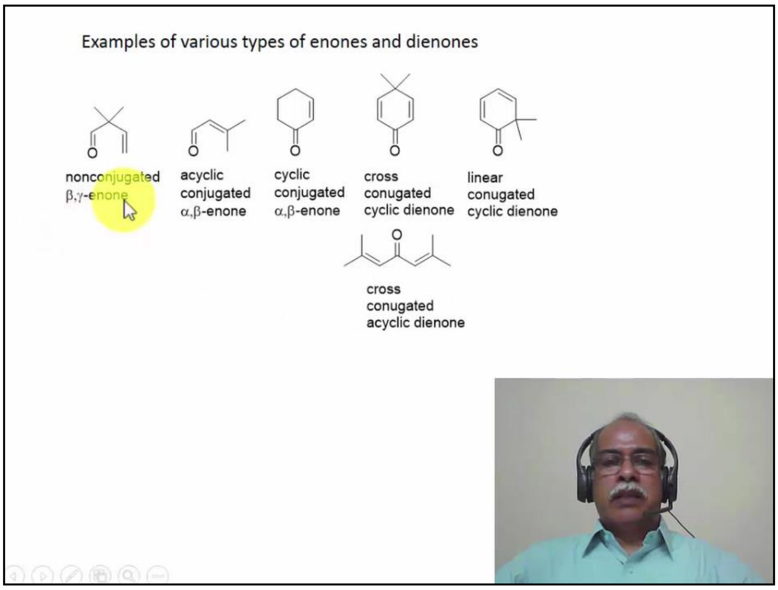

Examples of various types of enones and dienones

nonconjugated β,γ-enone

acyclic conjugated α,β-enone

cyclic conjugated α,β-enone

cross conugated cyclic dienone

linear conugated cyclic dienone

cross conugated acyclic dienone

Now, examples of various types of Enones and Dienones, are given here. This is a Non-Conjugated Beta Gamma Enone. In other words, the Carbonyl functional group, and the double bond, are not in conjugation. There is an, intervening SP3 hybridized Carbon, in this particular structure. This is an, Acyclic Conjugated Alpha Beta Enone. This is an Alpha Beta unsaturated compound, where the Carbonyl functional group, is in conjugation with the double bond. This is a cyclic version of the, Conjugated Alpha Beta Enone. This is Alpha and Beta. So, that is why, it is called, Alpha Beta Enone.

This is a Conjugated Cyclic system. This is a Cross Conjugated Cyclic Dienone. This is a Dienone. It is Cross Conjugated, for the simple reason that, this double bond here, and this double bond here, are not in direct conjugation. It is conjugated, through this particular Carbon, that is why, it is called a Cross Conjugated system. Unlike this particular system, which is Cross Conjugated system. If you look at this particular system, this is linearly conjugated. The entire double bonded system in the Carbonyl, are conjugated with respect to each other.

So, one can write a delocalized structure, all the way through, this particular system. This is an acyclic version of the, Cross Conjugated system. In other words, this double bond, and this double bond, are not in direct conjugation. It is conjugated, through this particular Carbon, which is part of the Carbonyl functional group. So, these are the various types of Enones and Dienones, we will consider for the discussion. The Photochemistry aspects of these molecules, is what we are going to look at, in a minute.

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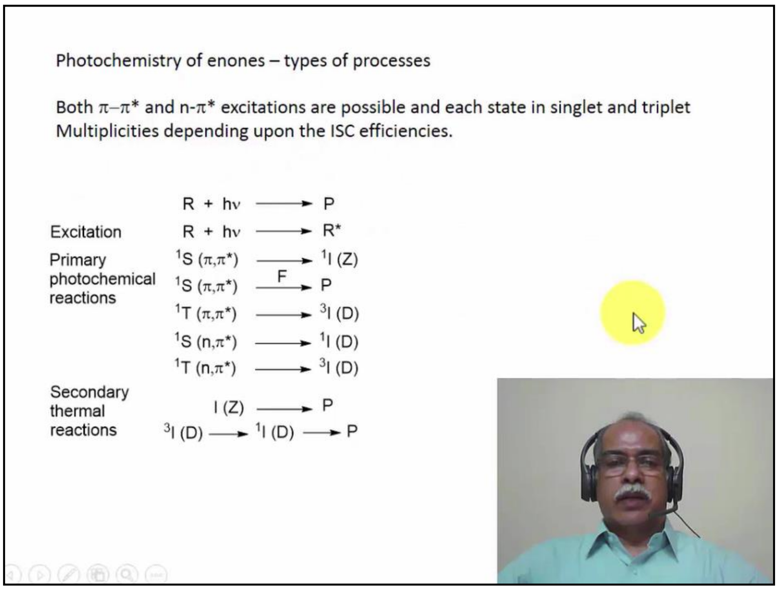

Photochemistry of enones – types of processes

Both $\pi-\pi^*$ and n-π^* excitations are possible and each state in singlet and triplet Multiplicities depending upon the ISC efficiencies.

$R + h\nu \longrightarrow P$

Excitation $R + h\nu \longrightarrow R^*$

Primary photochemical reactions
$^1S(\pi,\pi^*) \longrightarrow {}^1I(Z)$
$^1S(\pi,\pi^*) \xrightarrow{F} P$
$^1T(\pi,\pi^*) \longrightarrow {}^3I(D)$
$^1S(n,\pi^*) \longrightarrow {}^1I(D)$
$^1T(n,\pi^*) \longrightarrow {}^3I(D)$

Secondary thermal reactions
$I(Z) \longrightarrow P$
$^3I(D) \longrightarrow {}^1I(D) \longrightarrow P$

Now, the Photochemistry of Enone. The types of processes, that can take place, is given in this particular slide. Remember, in the case of Enone, you have both the PI system, which is a Carbon-Carbon-PI system, and the Carbon-Oxygen-PI system. So, there are two possible excitations. One can do, both the PI-PI-Star excitation of the double bond, as well as the N-PI-Star excitation of the Carbonyl bond. Both the excitations, are possible.

And, each state in the corresponding Singlet and Triplet multiplicities, are also possible, because it will depend upon the intersystem crossing efficiency, of course, which is predominating factor, whether it is a Singlet or the Triplet state, nevertheless, it is in principle possible, to access all the states by a Photochemical excitation. So, the processes, that we would like to discuss, in the case of the Photochemistry of Enone is that, the general reaction is the reactant, upon absorption of light, goes to the product.

The primary photo excitation process, is this one. This is reactant molecule, absorbing a photon, going to the excited state. The primary photo chemical state, the excited state can be a, first excited Singlet state, which is a PI PI-PI-Star state. From this first excited Singlet PI-PI-Star state, it can undergo reaction, to give the Photochemical reaction, to give an intermediate, which is a Singlet intermediate. And, this Singlet intermediate has a Zwitter ionic character, represented by Z.

In other words, it has some ionic character, associated with this. On the other hand, the first excited Singlet state, which is a PI-PI-Star state, can go to the product, through a funnel mechanism, essentially involving a Pericyclic pathway, without the involvement of any kind of an intermediate. The third option is that, the first excited Triplet state, which is a PI-PI-Star state, can go to a Triplet intermediate, which is a Diradical intermediate.

This Triplet Diradical intermediate, of course, will decay to the Singlet Diradical intermediate, before it goes to the process of forming the product, for example, which are secondary thermal reaction, which happens in these cases. Now, the corresponding Singlet Excited N-PI-Star state, and the Triplet excited N-PI-Star state, will produce the corresponding Diradical state.

From the corresponding Diradical state, the product will be formed by a decay process, that is shown here. So, these are all the possible mechanism by which, the Enones and Dienones can undergo the Photochemical reaction. Let us look at, some individual example, and go in depth of the mechanism, of some of this reaction.

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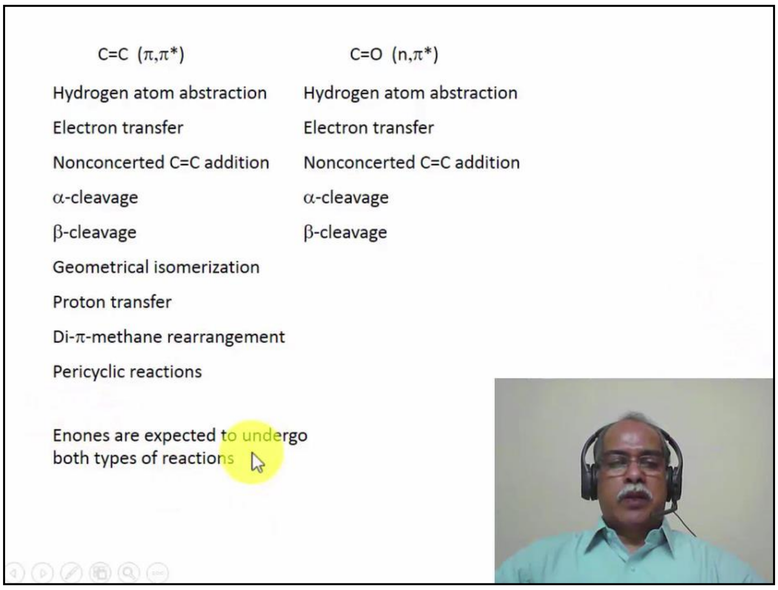

C=C (π,π^*)	C=O (n,π^*)
Hydrogen atom abstraction	Hydrogen atom abstraction
Electron transfer	Electron transfer
Nonconcerted C=C addition	Nonconcerted C=C addition
α-cleavage	α-cleavage
β-cleavage	β-cleavage
Geometrical isomerization	
Proton transfer	
Di-π-methane rearrangement	
Pericyclic reactions	

Enones are expected to undergo both types of reactions

Now, the C-PI-PI-Star excited state, and the N-PI-Star excited state, can undergo potentially, all these possible reactions. What are the reactions, the C-PI-PI-Star excited state undergoes? We have already seen, it can undergo Hydrogen Atom abstraction. Electron-Transfer reaction, so far, we have not seen. We will see it in another module, specifically devoted to, photo induced electron transfer process. It can undergo, Non-Concerted CC-Addition reaction, which we have seen, in the case of Paterno-Buechi reaction, for example.

Alpha cleavage, and Beta cleavages, are possible, in this PI-PI-Star excited state. Cis-Trans isomerization, is possible. We have seen, the Cis-Trans isomerization, in simple Olefinic system. We can apply that, to the Conjugated Enone systems also, in this particular case. Proton transfer is possible. We have not seen, any examples of Proton transfer. Di-PI-Methane rearrangement is possible, in this particular instance. Particularly, if it is a Non-Conjugated Ketone, it will undergo Di-PI-Methane rearrangement, through the PI-PI-Star process.

Many of the Pericyclic pathways are possible, when the Pericyclic process through the funnel mechanism, without the involvement of any kind of an intermediate. On the other hand, the N-PI-Star excited Carbonyl functional group, can undergo Hydrogen Atom abstraction. This is something, we have seen in the Norrish type two reaction, for example. Electron-Transfer reaction, we are yet to come across. In the future modules, we will see it. Non-Concerted CC-Addition reaction, can take place, for example.

Enone cycloaddition, is an example of that. Alpha cleavage, and Beta cleavages, are also possible, in the case of the N-PI-Star excited state. So, these are the common reactions, for both the states, PI-PI-Star, as well as the N-PI-Star state. These are the specific reaction, which the PI-PI-Star state will undergo, but the N-PI-Star state will not undergo, this reaction. In principle, the Enones are expected to undergo, both types of reactions. So, the Photochemistry of Enone, can be a fairly complex process, in the mechanistic details, and product distribution.

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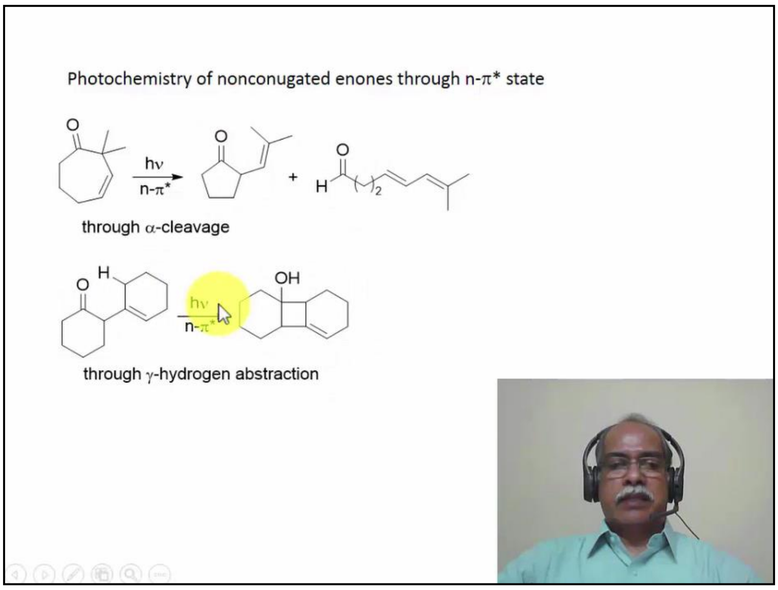

Photochemistry of nonconugated enones through n-π* state

through α-cleavage

through γ-hydrogen abstraction

Let us take the example of, this Non-Conjugated Ketone. This Non-Conjugated Ketone, can undergo for example, through an Alpha cleavage process. The Alpha cleavage, will produce an Allyl radical, in this particular case. The Allyl radical is a 1,5-Diradical. The 1,5, if you put the double bond here, and the radical center here, then it becomes a 1,5-Diradical. The 1,5-Diradical, undergoes ring closure reaction, to give the Cyclopentane, with this as the pendant group, in the form of a Vinyl group.

Alternatively, there is a Gamma Hydrogen available here. It can undergo, Gamma Hydrogen abstraction, to the Carbon here. So, the 1,5-Diradical, that is produced, undergoes the Gamma Hydrogen abstraction, followed by the rearrangement of the electrons, to give the Diene system, in this particular case. So, this Aldehyde, essentially comes from the Gamma Hydrogen abstraction, after the 1,5-Diradical is produced, in this particular instance.

Here is an example, directly, Gamma Hydrogen abstraction of the Non-Conjugated Ketone is taking place, followed by ring closure, to give this particular product. So, you can see a variety of reactions, are possible for the Enones, which are not conjugated, with respect to each other.

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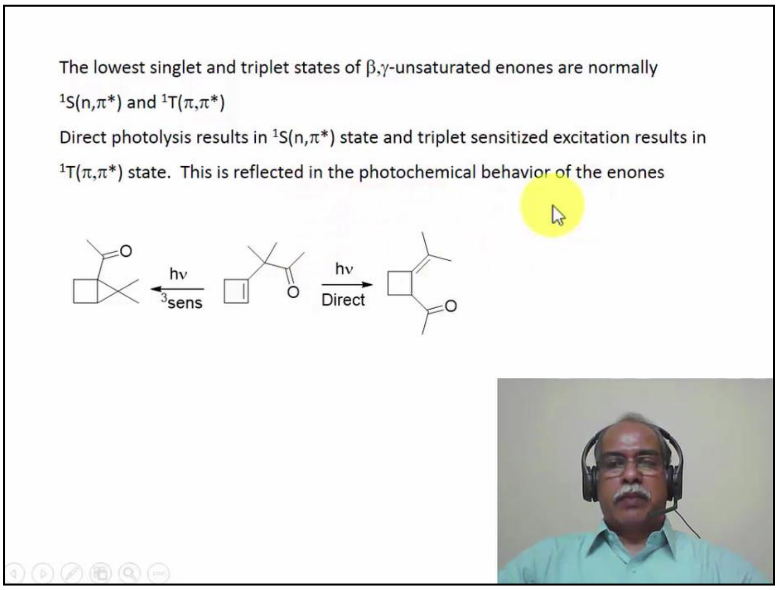

The lowest singlet and triplet states of β,γ-unsaturated enones are normally $^1S(n,\pi^*)$ and $^1T(\pi,\pi^*)$

Direct photolysis results in $^1S(n,\pi^*)$ state and triplet sensitized excitation results in $^1T(\pi,\pi^*)$ state. This is reflected in the photochemical behavior of the enones

Now, the state, whether it is coming from the N-PI-Star state of Singlet excited state, or the PI-PI-Star of the Triplet excited state, does make a difference, in terms of the kind of product, that is being formed here. This is a Non-Conjugated Ketone, nevertheless, it is an Alpha-Alpha-Disubstituted Non-Conjugated Ketone. In the direct photolysis, which will proceed through the excited Singlet state, N-PI-Star state, of the Carbonyl system, it will undergo Alpha fragmentation, followed by recombination, in the third position.

This is a 1,3-Shift, is what is taking place. So, 1,3-Shift product, essentially arises from the direct photo excitation, which produces the N-PI-Star excited state, of the Singlet state. On the other hand, if you use a Triplet sensitizer, it will undergo Triplet sensitization, to produce the PI-PI-Star Triplet excited state of the molecule. And, that will undergo a 1,2-Shift, which is an Oxa-Di-PI-Methane kind of a rearrangement.

Remember, Di-PI-Methane rearrangement, produces a Vinyl Cyclopropane. The Oxa-Di-PI-Methane produces, corresponding Oxa Cyclopropane, in this particular case. So, this is a Oxa-Di-PI-Methane product. This is a 1,3-Shift product, is what is formed. This will be coming from the Singlet Excited N-PI-Star state, whereas, this is coming from a Triplet PI-PI-Star state, in this particular instance. So, the electronic excited state reflects, the

Photochemical behavior of the Enone, in this particular case, of Non-Conjugated Ketone, of this kind.

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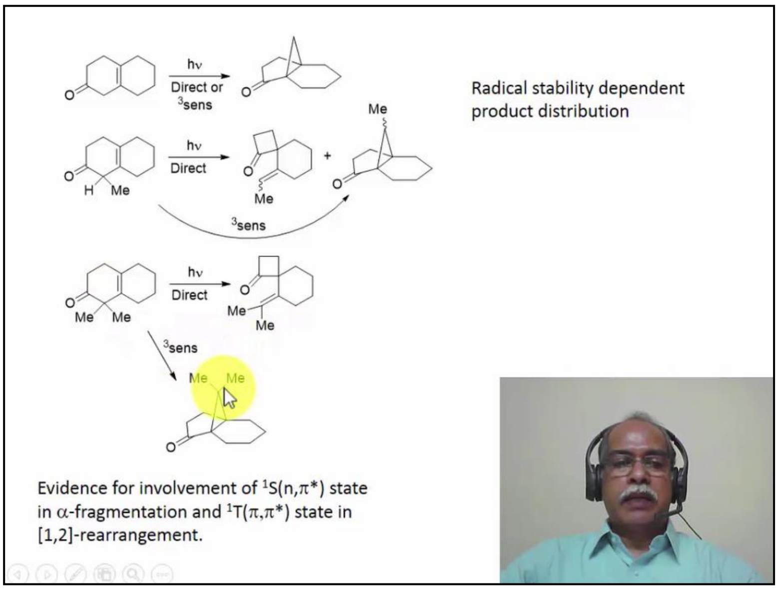

Radical stability dependent product distribution

Evidence for involvement of ${}^1S(n,\pi^*)$ state in α-fragmentation and ${}^1T(\pi,\pi^*)$ state in [1,2]-rearrangement.

These are also, examples of Non-Conjugated Ketones. These three examples are given, essentially to illustrate the point, that the radical stability, dependent on the product distribution. In other words, the product distribution is dependent on the radical stability, of the radical, that is produced. This will produce, a primary radical here, for example. This will produce a secondary radical, whereas, this will produce a Tertiary radical.

So, if you do a direct excitation, for example, where the primary radical is not stable, and it is not produced, then, whether you do a direct photolysis, or the sensitized photolysis, this molecule will essentially undergo Oxa-Di-PI-Methane rearrangement, 1,2-Shift is what is happening here, to produce a Cyclopropane, with the Vinyl derivative, which is part of the Carbonyl functional group here, for example. So, this is Oxa-Di-PI-Methane product, is what is formed here.

On the other hand, if you do the secondary fragmentation, producing a secondary radical, in this particular case. The secondary radical, that is produced, undergoes 1,4 recombination, to produce the Spiro-Ketone, producing this Exomethylene bond, and the Spiro-Ketone. This is a direct Alpha cleavage product, followed by a recombination, that is taking place. Whereas, this is a mixture of product, that is formed, when it is directly photolyzed.

On the other hand, sensitized photolysis gives, only the Oxa-Di-PI-Methane rearrangement product. When it comes to a radical, that is stable, which is a Tertiary radical, direct photolysis gives the Alpha cleavage, followed by 1,4-Diradical recombination. Whereas, the

Triplets sensitized reaction, going through a Triplet PI-PI-Star excited state, specifically produces only the Di-PI-Methane rearranged product.

So, whether the Di-PI-Methane rearranged product will be formed, or a mixture of product will be formed, it is controlled by the stability of the radical produced, in this. The most stable radical is produced, in the direct photolysis. So, it undergoes Alpha cleavage, followed by 1,4-Diradical recombination, in this case. The Triplet excited state, it undergoes a totally a different reaction, which is the Oxa-Di-PI-Methane rearranged product, in this case.

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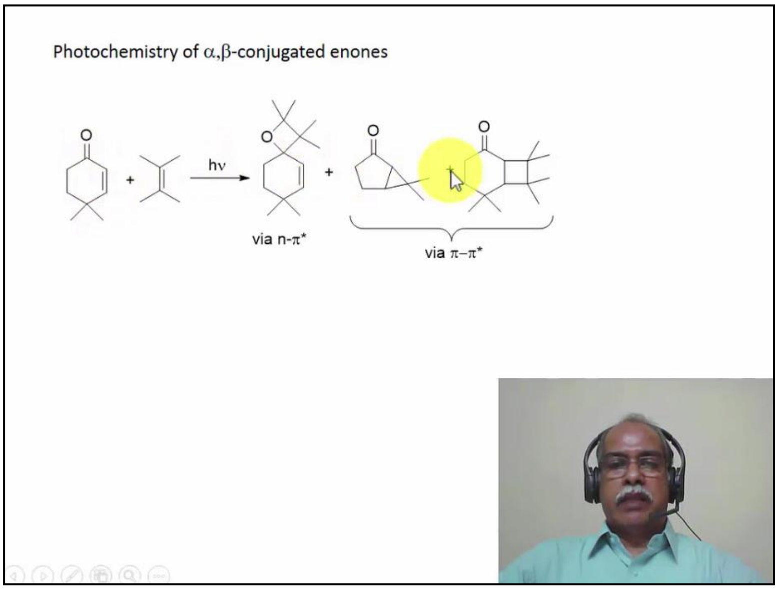
Photochemistry of α,β-conjugated enones

Now, the Photochemistry of Alpha Beta Unsaturated Ketone, is what is given here. In this particular instance, there are three products formed here. The first product is a Oxetane formation, which is a Paterno-Buchi kind of a reaction, which arises essentially from the N-PI-Star excited state of the Carbonyl functional group. On the other hand, from the PI-PI-Star state of the Carbonyl functional group, via a Triplet sensitizer, for example.

It can undergo, Oxa-Di-PI-Methane rearrangement, which is this particular product. Or, it can undergo a 2+2-Cycloaddition reaction, which is this particular product. You can see here, either an Oxetane can be formed, or a Cyclobutane can be formed, depending upon, whether the 2+2-Cycloadditions takes place, across the Carbonyl double bond, or the CC double bond, giving this two type of product. This is a unique product, coming from the Oxa-Di-PI-Methane rearrangement.

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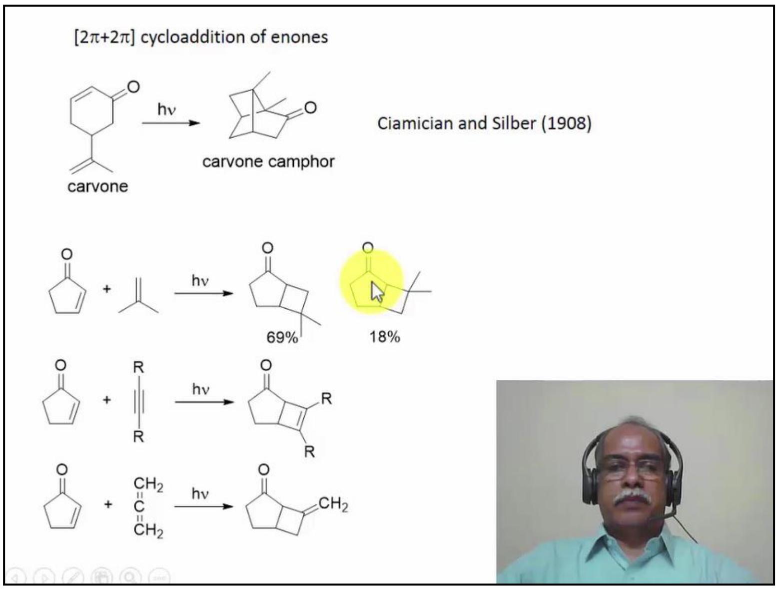
[2π+2π] cycloaddition of enones

Ciamician and Silber (1908)

Now, the photo cycloaddition reaction, is a very old reaction. It is more than 100 years old, for example. It was initially discovered by, Ciamician and Silber, in Italy. So, in the Italian sunlight, they left the flask containing Carvone, into the Italian sunlight, in their balcony of their laboratory. And, they observed, this transformation of Carvone, transforming into Carvone Camphor. You can see here, this double bond, and this double bond, has undergone a cycloaddition process. Such a cycloaddition process, is possible only through a boat type of a confirmation.

Because, the accessibility of this double bond, to this double bond, in a chair confirmation, would be impossible. So, through a boat type of a conformational change, this will undergo the 2+2-Cycloaddition reaction, to produce the Carvone Camphor, which is a nickname for this particular compound. Cyclopentenone is known to undergo, 2+2-Cycloaddition reaction, by direct photolysis, to produce two Regio isomers, depending upon, how this Gem Dimethyl Isobutylene is oriented, with respect to this double bond, these two products are possible.

In the case of Symmetrically disubstituted Acetylene, only one product is possible, which is a Cyclobutene fused with a Cyclopentenone ring, in this particular instance. Allene also undergoes, 2+2-Cycloaddition reaction with the Cyclopentenone, resulting in the formation of an Exomethylene substituted Cyclobutane, fused to the Cyclopentenone derivative, as it is shown here.

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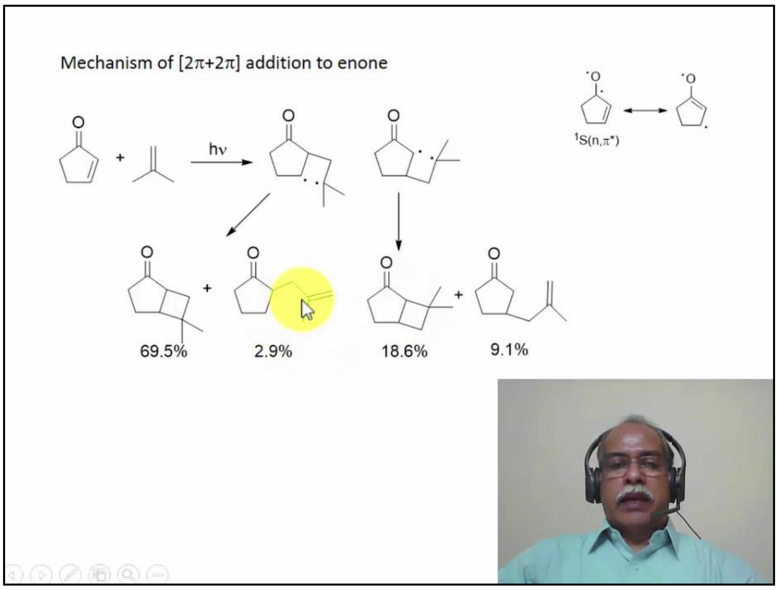
Mechanism of [2π+2π] addition to enone

The mechanism of the 2+2-Cycloaddition reaction, is what is shown here. If you consider, the N-PI-Star excited state of the Carbonyl functional group, you can consider it as a Diradical, which is a 1,2-Diradical, or you can consider it, as the 1,5-Diradical, as it is shown here. 1-2-3, 1,4-Diradical, as it is shown here, for example. Now, the Photochemical cycloaddition produces predominantly, this particular isomer of the molecule.

That is explained, on the basis of the formation of this Diradical, or this Diradical intermediate. Between, these two Diradical intermediate, this Diradical intermediate is going to be more stable, for example. Because, of the fact that, this is a Tertiary radical, and this is a radical away from the Carbonyl functional group. So, this is a Reductively more stable, compared to this particular Diradical intermediate.

So, from this Diradical intermediate, one can do Hydrogen transfer to this, from the Methyl group, to the Gamma Hydrogen. Alpha-Beta-Gamma-Delta Hydrogen transfer, can take place to this particular Carbon, producing the Olefin, in minor amount. Recombination of the 1,4-Diradical, to form a sigma bond, produces the Cyclobutane, fused to the Cyclopentanone. So, the Regio isomer, this is the major Regio isomer, compared to this Regio isomer. The Hydrogen abstraction products, are also formed to a smaller extent, in this particular case.

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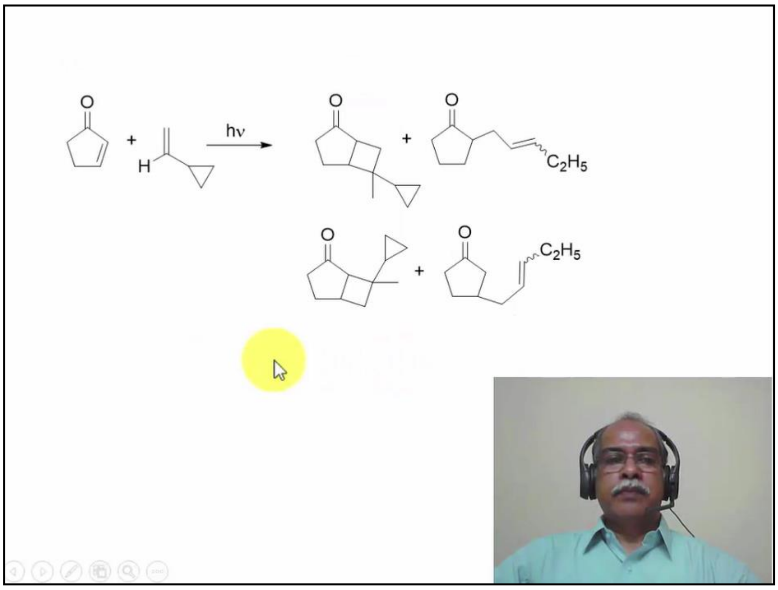

The fact that, the 2+2-Cycloaddition reaction, proceeds through a radical intermediate, is shown by way of, taking a Cyclopropyl substituted Olefin. Remember, if the Diradical produced, is having this particular Diradical structure, that will be a Cyclopropyl Methyl radical kind of a thing, which will undergo ring opening, to give Butenyl radical. The Butenyl radical, will now essentially produce the Olefin, ring opened product.

So, both the Cyclobutenyl product is formed, as well as the ring opened product is formed, indicating the Diradical intermediate being formed, in this particular case, which is a radical, which is Alpha to the Cyclopropyl ring. So, the Cyclopropyl ring, undergoes the ring opening reaction, to produce the Butenyl radical, which is part of the structure, that is shown here, in this Olefinic product, that is shown here.

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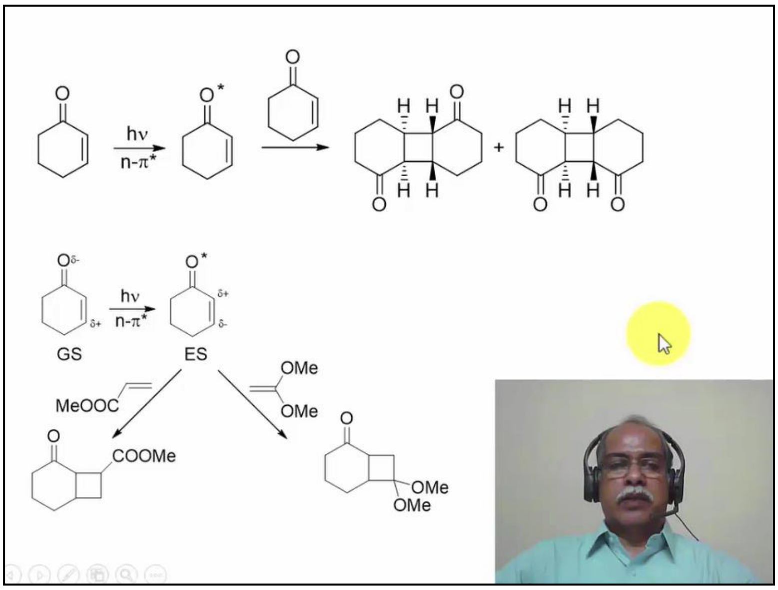

Cyclohexanone itself, undergoes 2+2-Cycloaddition reaction, with itself. N-PI-Star excited state of Cyclohexenone, can be represented as a Umpolung kind of a character, in the ground state, for example. This is an electron deficient Carbon, and this is an electron rich Oxygen, because of the delocalization of electron, in this direction. On the other hand, once the N-PI-Star excitation takes place, the Oxygen is depleted of electron. Whereas, the PI-Star state of the Olefinic bond, is increasing in electron density.

So, this is now having a higher electron density. The Carbonyl Oxygen, and the Alpha Carbon, have a lower electron density, which is essentially, the reversal of polarity, of this excited state molecule. The Cyclohexenone, undergoes 2+2-Cycloaddition reaction, to give Head-to-Head Dimer, which is a Cis-Anti-Cis kind of a compound. Also, it produces a Head-to-Tail kind of a compound, which is also a Cis-Anti-Cis kind of a product. It depends, on the relative orientation of the two molecules, in the excited state, and the ground state.

The excited state molecule, with the ground state molecule, producing these two type of Head-to-Head, as well as the Head-to-Tail Dimer, that is photo Dimer, that is being formed here. Now, whether the excited state, reacts with an electron rich Olefin, or an electron poor Olefin, decides the Regio chemistry of the reaction. If for example, in this particular instance, the Regio isomer formed is, this is a major Regio isomer, that can be easily explained by the fact, this Carbon is an electron rich Carbon.

So, that gets attached to the electron deficient Carbon. Whereas, this is an electron deficient Carbon, with the two Oxygens, in this particular position. So, that gets attached, to the electron rich Carbon. So, this is a major product, that is formed. The opposite Regio isomer is formed, when you have an Alpha Beta Unsaturated Ester, of this kind. This is an electron deficient Carbon, that gets attached to the electron rich Carbon, in this particular case, like a Michael addition kind of a process.

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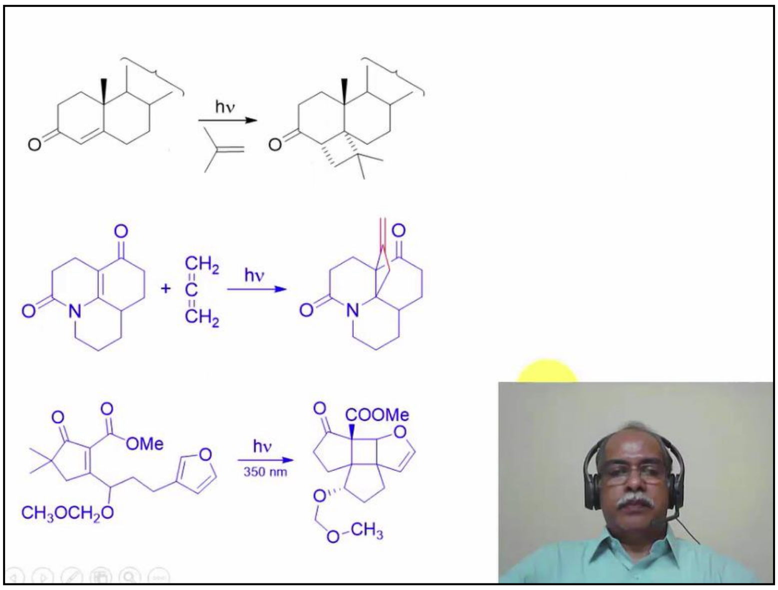

These are some synthetic examples of, Enone cycloaddition reaction. Enone Isobutylene, undergo cycloaddition reaction to this Enone, producing the Endo cyclic compound, which is the Cyclobutane fused Cyclohexanone derivative, in this particular case. This Ene-Amino Ketone, undergoes the cycloaddition process, with Allene. And, the Red portion, correspond to the Allene, for example.

The Exomethylene, is coming from the additional Methylene, that is present in Allene. The reaction takes place, across this Carbon-Carbon double bond, to produce the Cyclobutane ring, in this particular case. Here, a Furan is undergoing a 2+2-Cycloaddition reaction, intramolecular version of 2+2-Cycloaddition reaction, wherein this 5-Membered ring, is essentially produced, because of this pendant group, that is here.

So, the reaction center, is this particular double bond, reacts with this double bond here, producing the Cyclobutane formation, with a Carboxylic acid substituent, in this particular position. This molecule, could be used for example, in the synthesis of some Terpenoid kind of a molecule. And, that makes this transformation, an interesting, and important transformation.

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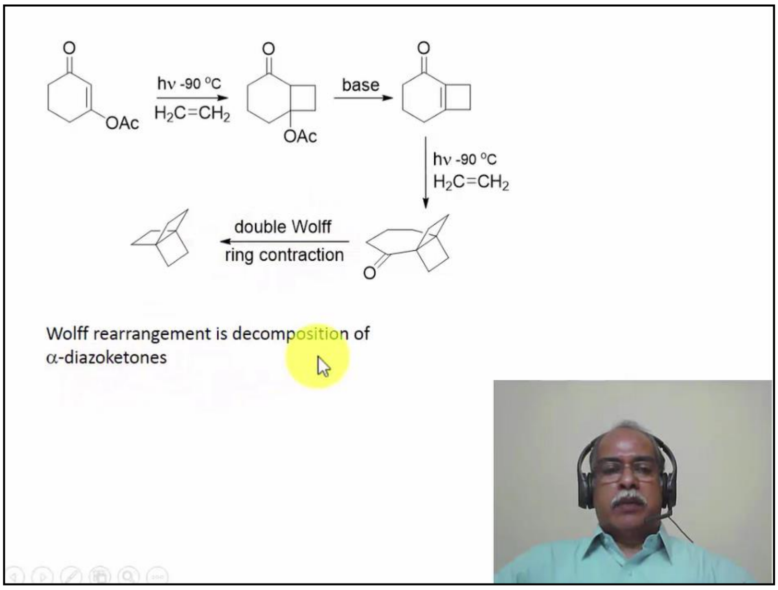

Wolff rearrangement is decomposition of α-diazoketones

This kind of propeller shaped molecule, can be synthesized, by Enone cycloaddition reaction. This is the Acetoxy derivative, of Cyclohexa-1,3-Dione. Cyclohexa-1,3-Dione Enol form is acetylated, to produce the Acetate. And, that undergoes at a very low temperature, photo cycloaddition with the Ethylene, to produce a Cyclobutane fused molecule. And, under the basic condition, one can eliminate Acetic acid, to produce again, the Olefin Cyclohexenone.

This will further, undergo reaction with the Ethylene, for example, to produce this bridged propeller shaped molecule. Now, all you need to do is, to do a double Wolf rearrangement, to get rid of two of the Carbons, which are excess Carbon, to produce the 2,2,2-Propylane, which is this particular molecule. We will come across, the double Wolf rearrangement, or in general, the Wolf rearrangement, which is a decomposition of Alpha Diazo Ketone, in the later stage of the modules.

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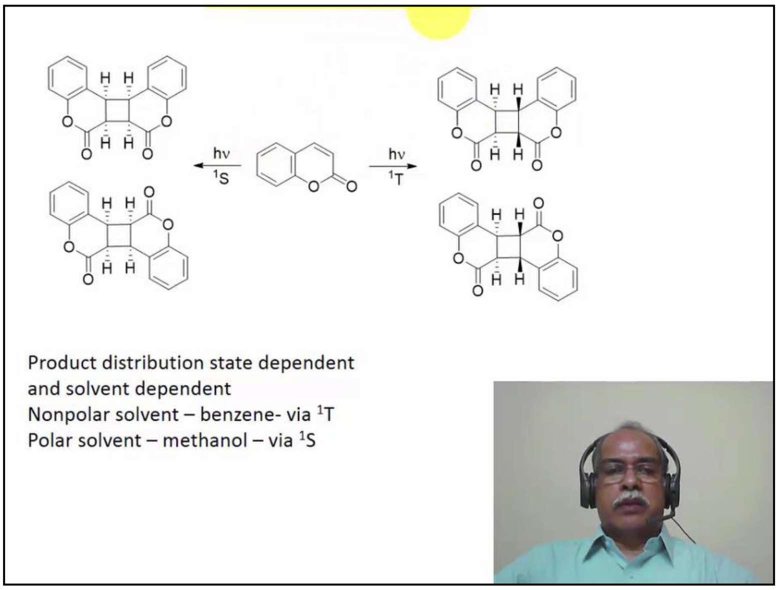

Product distribution state dependent and solvent dependent

Nonpolar solvent – benzene- via ^{1}T

Polar solvent – methanol – via ^{1}S

Here is an example of Coumarin, undergoing photo cycloaddition reaction. This is electronic state dependent, whether it is a Singlet state, or a Triplet state reaction. The Singlet state reaction, is essentially coming from direct photolysis. The Triplet state reaction, is via a polarity solvent, also plays a major role in the product distribution. Because, it is state dependent. And, one can either sensitize the reaction, or do it in a Non-Polar solvent, to go through the Triplet excited state.

What is important is, in the case of Singlet excited state, you form the Cis-Cyn-Cis isomer. In other words, it is as if, this two rings are PI stacked, with respect to each other, before it undergoes a cycloaddition reaction. It could very well be that, it is going through an excimer kind of an intermediate, in this particular case. And, here again, this is PI stacked, except that, it is a Head-to-Tail kind of a Dimer, this is a Head-to-Head kind of a Dimer, Cis-Cis-Cis is the stereochemistry, as far as the ring junctions are concerned.

In the Triplet excited state, for example, this is like an Exo kind of an approach, where you have a Head-to-Head, as well as Head-to-Tail approach, except the stereo chemistry now, here is Cis-Anti-Cis kind of a stereochemistry, is what is formed. Coumarin have a, very rich Topochemical Photochemistry also. In the solid state also, they undergo 2+2-Cycloaddition reaction, to produce the photo Dimer of the Coumarin, that is shown here.

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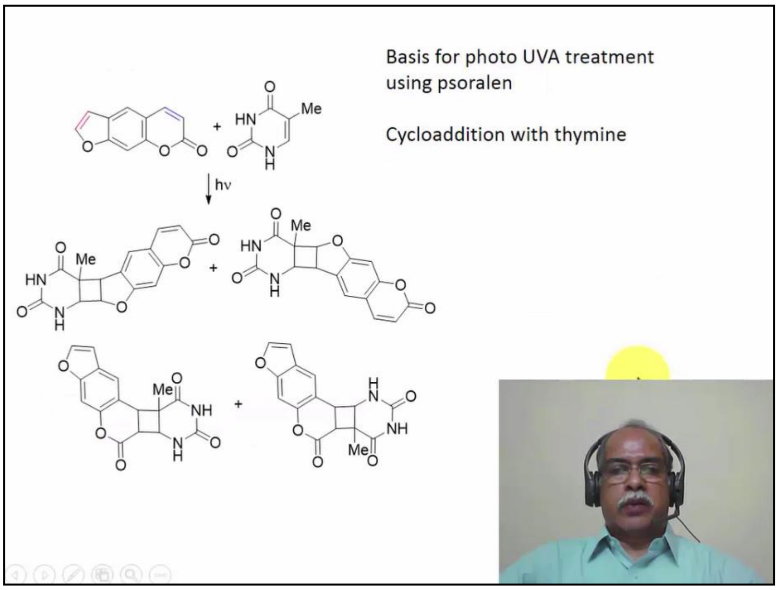

Basis for photo UVA treatment using psoralen

Cycloaddition with thymine

Now, Psoralen, which is actually this particular molecule, has two double bond. One is indicated in the Red color, the other one is indicated in Blue color. This slide, essentially tries to give the Photo Physics, or Photochemistry, involved in the UV treatment of certain cancer, for example. The basis for the UV photo treatment, of the using Psoralen, is what is explained in this transparency. Essentially, it undergoes cycloaddition reaction with Thymine, which is the constituent of a DNA molecule.

So, this is a model reaction, that essentially indicates to us, how to suppress the reproduction of DNA, or replication of DNA, by means of cycloaddition process, that takes place here. Now, the cycloaddition product in principle, can result in the photo cycloaddition here, or photo cycloaddition here, depending upon, which double bond is reacted, producing two types of Head-to-Head, or Head-to-Tail kind of an isomer, is what is being produced, in both cases.

Photo cycloaddition with this double bond, essentially produces these two molecules, leaving the other double bond intact. Whereas, the photo cycloaddition, with this double bond, essentially produces these two molecules, leaving the other exocyclic, the Benzofuran double bond intact, in this particular case. So, these are the chemical reactions, that are responsible for the consumption of the Thymine, which is responsible for the photo UVA treatment, using the Psoralen, which is this particular molecule, in this case.

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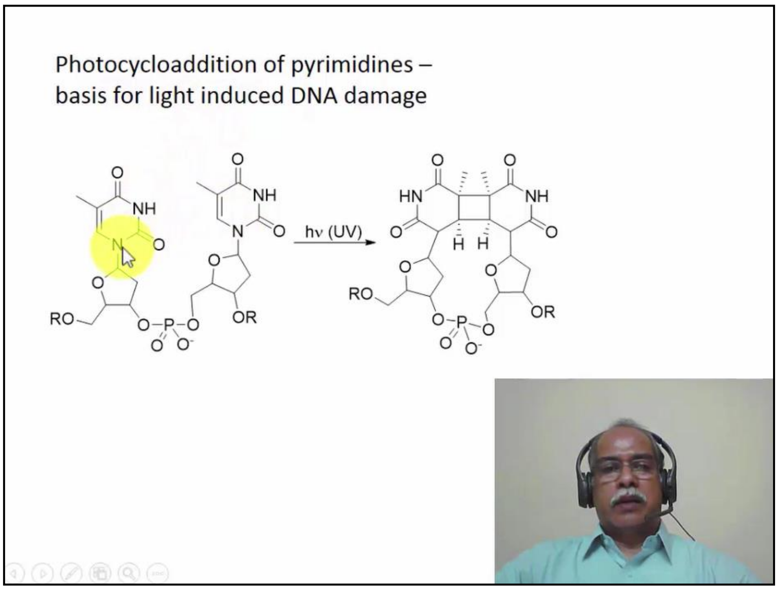

Photocycloaddition of pyrimidines – basis for light induced DNA damage

The mechanism of photo cycloaddition, is what is proposed, for the light induced damage of DNA. For example, certain skin cancer can take place, because of the mutation of DNA, because of direct exposure to ultraviolet radiation of the sunlight, for example. So, without Sun protection, if you are going to the Beach, it is likely to that, your skin gets damaged. It can lead to Skin Cancer, some kind of a Skin Carcinoma, for example. And, the model system, that is shown to undergo, this 2+2-Cycloaddition reaction.

When, this Pyrimidine units are directly photolyzed, they undergo the 2+2-Cycloaddition reaction. This will be like, a mutated DNA kind of a structure, is what it will produce, for example. So, this is a basic, try to understand the basic principle behind the, light induced DNA damage, which is essentially caused by the, two Pyrimidine units, undergoing a 2+2-Cycloaddition reaction, to form a photo Dimer, which could be responsible for the DNA damage.

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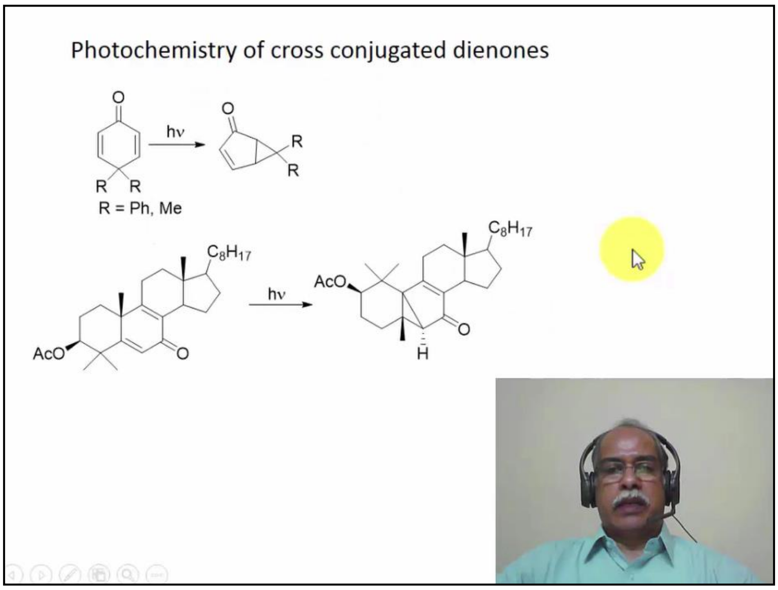

Photochemistry of cross conjugated dienones

Now, let us move on to, the Photochemistry of Cross Conjugated Enone. Cross Conjugated Enones, have a propensity to undergo, Di-PI-Methane kind of a rearrangement. That mechanism, is shown in the next slide, for example. So, this is essentially a 1,2-Shift kind of a product, is what is obtained, with the formation of a Vinyl Cyclopropyl derivative, in this particular case.

The same reaction is shown here, in a steroidal system of Cyclohexadienone system, undergoing a 1,2-Shift, to give the Cyclopropyl Vinyl derivative, which is a Di-PI-Methane rearrangement product, in this particular case.

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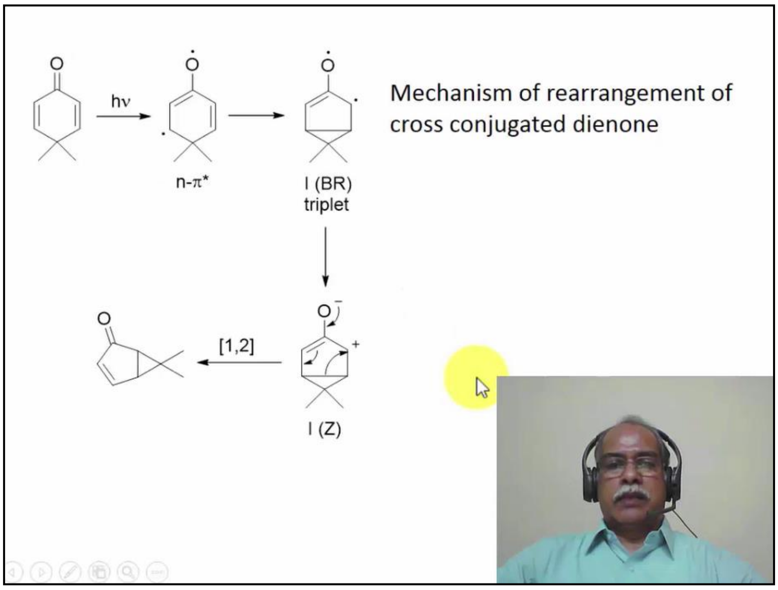

Mechanism of rearrangement of cross conjugated dienone

The mechanism, is shown here. This is proposed by Zimmerman. The mechanism involves, the N-PI-Star excitation, to produce the Diradical intermediate. The Diradical intermediate, essentially undergoes a ring closure, to produce a Cyclopropyl radical intermediate. This is, now a Biradical Triplet intermediate, which relaxes to a Zwitter ionic intermediate, in the ground state.

The Zwitter ionic intermediate, essentially undergoes this rearrangement, that is shown here, forming this Cyclopropane annulated Cyclopentenone, for example, by a 1,2-Shift, as shown, indicated by the arrow here, for example, in this particular instance. So, this is a bond, that breaks and swings around, to form the bond over here. This bond, does not break. There is a mistake here. It is either this bond, or this bond, has to break and swing around, and recombine at this position, in this particular case.

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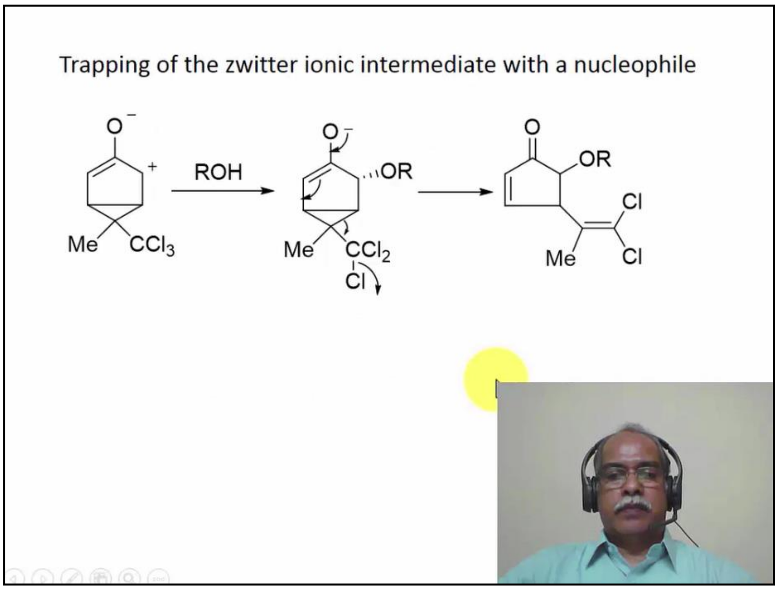

Trapping of the zwitter ionic intermediate with a nucleophile

The Zwitter ionic intermediate, which is proposed in this mechanism, has evidence arising by the trapping, using a nucleophile. When alcohol is used as a nucleophile, external nucleophile for example, it traps the Zwitter ionic intermediate, by Protonation, followed by nucleophilic addition, to this particular Carbonium ion center. The Enolate, essentially undergoes this elimination process, to produce this.

This is, one of the products formed, when a Trichloro Methyl substituent is present in the Conjugated Enone. In other words, if one of the Methyl group is a Trichloro Methyl group, and if one does the photolysis, this is one of the products formed, in the presence of an alcohol, produced by the trapping of the Zwitter ionic intermediate, by the nucleophile, which is the alcohol, which produces this molecule.

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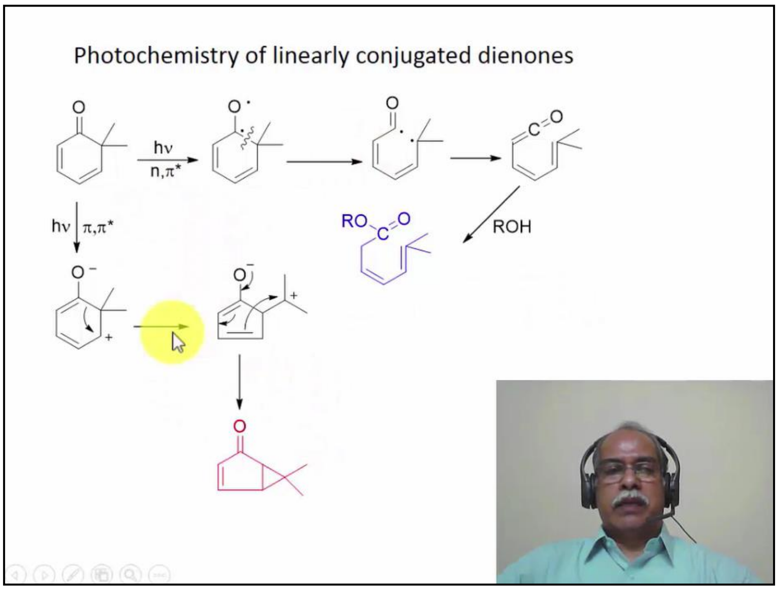

Photochemistry of linearly conjugated dienones

Photochemistry of linearly conjugated Dienones, is what is shown here. The linearly conjugated Dienone, essentially produces this Beta Gamma Delta unsaturated Dienoic acid, is what is produced. And, the Di-PI-Methane rearrangement product is also formed, depending upon, whether you do a direct photolysis to go to the N-PI-Star excitation, or a Triplet sensitized PI-PI-Star excitation, of this kind.

So, direct PI-PI-Star excitation, essentially produces a Zwitter ionic intermediate of this kind, resulting in the formation of this product, this Zwitter ionic intermediate, which undergoes the rearrangement, to give this particular product, which is essentially the equivalent to a Di-PI-Methane rearrangement kind of a product, is what is formed here.

On the other hand, the N-PI-Star excitation, can produce an Alpha fragmentation. The Alpha fragmentation product, is essentially a Ketene, which is shown here, which can be trapped with an alcohol, to produce the corresponding Ester. So, these are the two major pathways, by which the cyclic conjugated, linearly conjugated Dienone, undergoes the Photochemical reaction.

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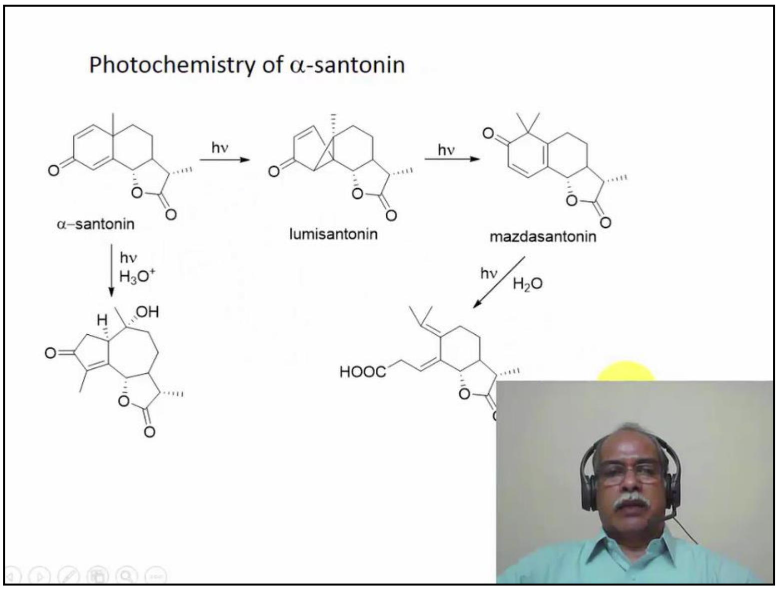

Photochemistry of α-santonin

The cyclically conjugated, Cross Conjugated system, for example, beautiful example, is a Photochemistry of Alpha-Santonin. Alpha-Santonin is a naturally occurring Terpene molecule, which on photolysis, gives a photo isomerization product, which is called the Lumi-Santonin.

Lumi-Santonin, further undergoes Photochemical isomerization. This is similar to an Oxa-Di-PI-Methane rearrangement, which undergoes 1,2-Rearrangement, to give the cyclic linearly conjugated system, which undergoes the Alpha fragmentation, followed by Ketene formation, and trapping with water. Just like, it is shown here, Ketene formation and trapping with alcohol.

Here, Ketene formation, trapping with water, produces the corresponding Carboxylic acid. On the other hand, this under acidic condition, when Alpha-Santonin is photolyzed, the Protonated compounds essentially undergoes this reaction, to produce this particular skeleton, in this case.

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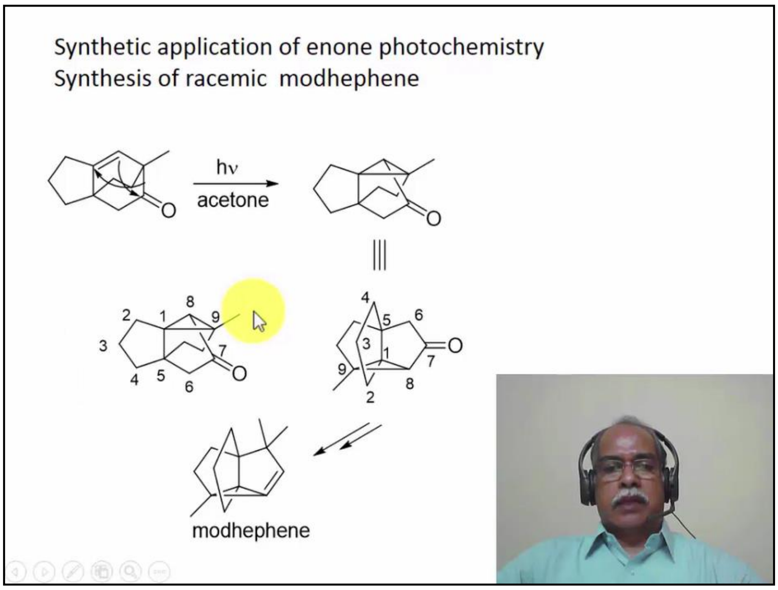

Synthetic application of enone photochemistry
Synthesis of racemic modhephene

Again, synthetic application of Enone Photochemistry, is illustrated by the synthesis of a racemic Modhephene. Modhephene is a Terpenoid molecule, essentially coming from this particular Ketone, which is a non-conjugated Ketone, for example, undergoing a 1,2 kind of a shift, as it as shown by the arrow, to produce the corresponding Oxa-Di-PI-Methane rearranged product. This structure is same, as this structure. Or, this structure is identical, to this particular structure. If you follow the numbering, starting from the bridgehead, 1-2-3-4-5-6-7 Carbonyl.

And, then the 8 and 9, are the connectivity, that you have here. So, after 9, this is 10 and 11, which is not numbered. So, you can go from here, one, the bridgehead. 1-2-3-4-5-6-7-8-9-10-11. So, the same skeletal arrangement, is what is shown here, in terms of the connectivity. And, this is Modhephene, which is a Terpenoid molecule. The basic skeleton is essentially, obtained by a Photochemical Oxa-Di-PI-Methane rearrangement, is what is illustrated. Further transformation, of this molecule to Modhephene, was carried out in the laboratory.

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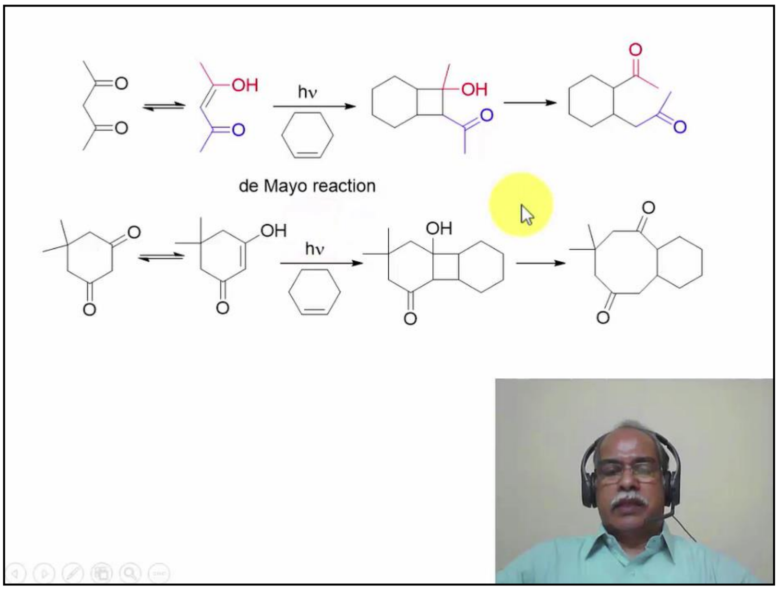

This particular reaction is called, DeMayo reaction. Essentially, the Red part of the molecule, and the Blue part of the molecule, is fragmented, and attached, across the Carbon-Carbon double bond here, overall reaction, if you look at. What is this molecule? This is nothing but, the Enolic form of the Acetyl Acetone. This is Acetyl Acetone. The Enolic form of Acetyl Acetone, has a double bond. When, it is photolyzed in the presence of Cyclohexene, the Carbonyl excitation essentially, is what is happening.

This is a Conjugated Enone system, undergoing 2+2-Cycloaddition reaction, to produce this molecule. If you look at this molecule, this is Alpha-Beta, Beta Hydroxy Carbonyl compound, which is nothing but, an Aldol compound. So, this double bond has undergone 2+2-Cycloaddition reaction, with this double bond here, producing the Cyclobutane fused Cyclohexane, in this particular case.

And, the Red portion, and the Blue portions, are essentially delineated, showing that the Red portion, and the Blue portion, are added across the double bond, in this particular instance. One can do a Retro Aldol reaction. This is an Aldol condensation product. So, under basic condition, Retro Aldol reaction, can take place. Anion generated here, undergoes a ring opening reaction of the Cyclobutane, producing this particular Diketone, that is shown here.

So, you see exactly, you have fragmented the molecule here, attached the Red portion onto 1-Carbon, attached the Blue portion on to the other Carbon, across the Carbon-Carbon double bond. A beautiful reaction, in terms of the synthetic utility of producing, 1,5-Diketones of this type, by a simple 2+2-Cycloaddition, Retro Aldol reaction, in this case. Here is another, the same molecule, same reaction with another molecule. This is Dimedone. Dimedone Enol form, for example, produces the Enol, which is shown here.

2+2-Cycloaddition reaction, of the Enol with Cyclohexene, produces here. Retro Aldol reaction, now gives a beautiful Cyclooctadiene kind of a molecule, beautiful synthetic examples of the DeMayo reaction, that is shown here. So, what we have seen, in this particular module, is the Photochemistry of Enones, and Dienones, of various kind. Conjugated, Non-Conjugated, Cross Conjugated, linearly conjugated, these are the four different systems, that we have seen.

We have seen, that the reaction is highly dependent upon, whether the reaction proceeds from the Singlet excited N-PI-Star state, or Triplet excited PI-PI-Star state, the spin states seem to matter, in some of these reactions, very much. And, these are some of the examples, illustrate the dependency of the reaction mode, on the spin state of the excited state. I hope, you enjoyed this module. Thank you very much, for your kind attention.