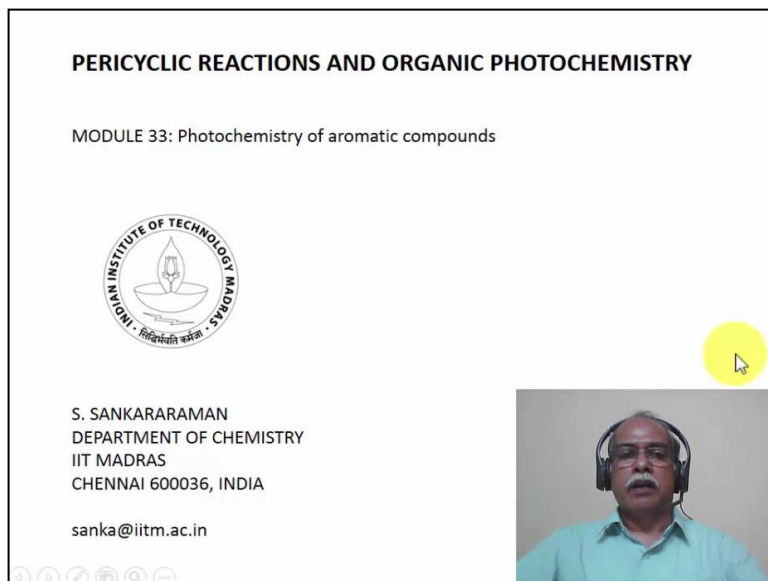


**Pericyclic Reactions and Organic Photochemistry**  
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**Module No. #08**  
**Lecture No. #33**  
**Photochemistry of Aromatic compounds**

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**PERICYCLIC REACTIONS AND ORGANIC PHOTOCHEMISTRY**

MODULE 33: Photochemistry of aromatic compounds

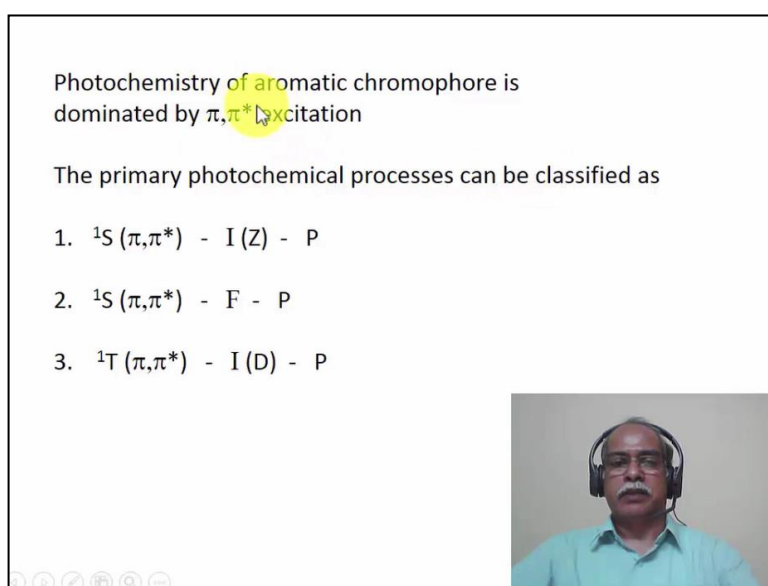


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Hello, welcome to the online course on, Pericyclic Reactions and Organic Photochemistry. We are in Module Thirty-Three, now. This is the Module, concerning the Photochemistry of Aromatic Compounds. Aromatic Compounds are, PI electron rich compounds.


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Photochemistry of aromatic chromophore is dominated by  $\pi, \pi^*$  excitation

The primary photochemical processes can be classified as

1.  $^1S(\pi, \pi^*) - I(Z) - P$
2.  $^1S(\pi, \pi^*) - F - P$
3.  $^1T(\pi, \pi^*) - I(D) - P$

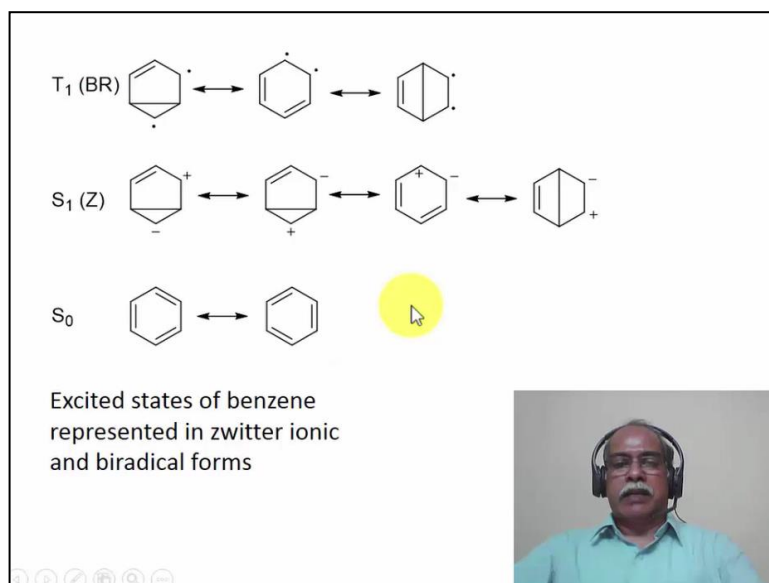


So, their Photochemistry is reaching, PI-PI-Star excitation processes. If you take Benzene itself, it has absorption in the range of, 180 to 200 Nanometers, one set of bands, 200 to 220, another set of bands, from 220 to 250, another set of bands. All of them are PI-PI-Star excitation band, corresponding to electronic excitation, going from  $S_0$  to  $S_1$ , and  $S_2$  states as the, wavelength decreases, the energy increases, corresponding to the excitation.

The primary Photochemical process of Benzene, and its derivatives can be, classified as follows. From the, first excited Singlet state, which is a PI-PI-Star state, one can expect intermediate, which are Zwitter ionic in nature. And, the Zwitter ionic intermediate, once they are formed, it goes to the final product. There is a definite evidence, for the involvement of Zwitter ionic intermediate, which are done by trapping experiment.

The first excited Singlet state, which is a PI-PI-Star excited state, can also go through a funnel mechanism, which is a concerted mechanism, to go to the product, without the involvement of any kind of intermediate. Finally, Triplet excited state, PI-PI-Star state, can also go through an intermediate stage, which is a Diradical state, resulting in the product formation. We will see examples, of each one of this case, in the coming slides.

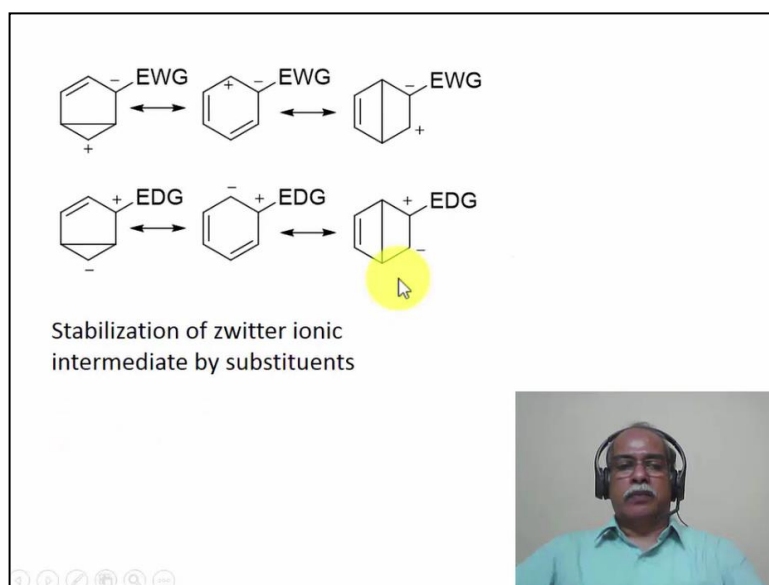
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So, this is a schematic representation of, what is said, in case of the schemes here. The  $S_0$  state, is essentially the ground state, Benzene state, which is a canonical structure, are written here. The first excited Zwitter ionic state, is essentially 1,3-Dipole kind of a state, or 1,2-Dipole kind of a state, as indicated here. These are all, resonant structures of each other. And, the Triplet state is a Biradical state.

Biradical state is also represented as, either 1,3-Biradical state, or 1,2-Biradical state, and so on. The reason, this kind of a bridged bicyclic system, Diradical state is given, there are products, which are arising out of the Biradical intermediates of this type, as well as Zwitter ionic intermediates of this type, which we will see, in the due course of this particular module.

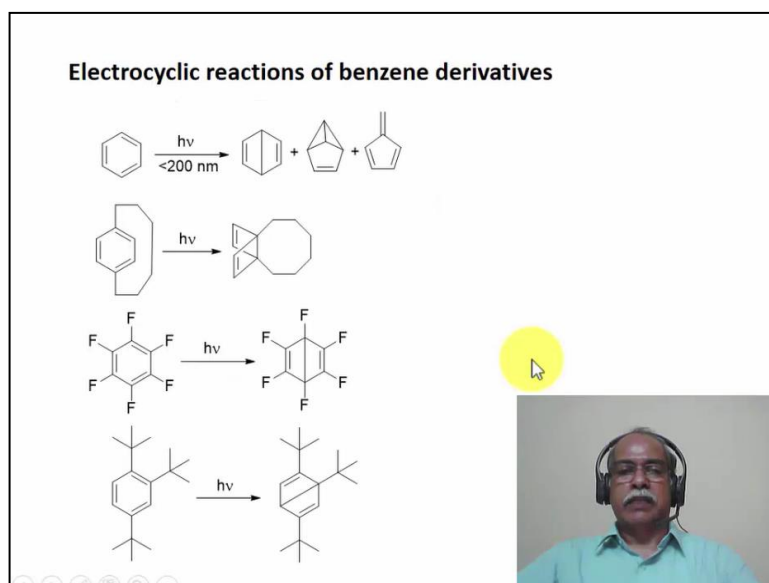
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Now, whenever you have a strongly electron withdrawing functional group, like the Nitro functional group, Cyano functional group, Ester functional group, and so on, the Zwitter ionic intermediate is favored in this manner, such that, the Anionic charge is close to the electron withdrawing functional group. This is understandable. Because, the Anionic charge will be stabilized, by the electron withdrawing functional group, by delocalization process.

Similarly, when there is a strong electron donating group, like the Methoxy group, or the Amino functional group, it is the cation of the Zwitter ion, is close to the electron donating functional group. Because, electron donating functional group, can stabilize the cationic charge, by delocalization process. And, there is again evidence to show, that this kind of Zwitter ionic intermediates are formed, during the course of the Photochemical reactions, of Benzene derivatives.

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Now, let us go into the various types of reactions, that Benzene can undergo. When Benzene is photolyzed, in less than 200 Nanometer regions, which is a vacuum ultraviolet region, for example, this would have essentially correspond to, excitation from the  $S_0$  state to  $S_2$  state. So, the resulting Photochemistry, actually could be arising from the  $S_2$  state, in this particular case. A mixture of compounds, are formed. All of them are, isomers of Benzene, for example.

This is Dewar Benzene. This is Benzvalene. And, this is Fulvalene. These three products, can be formed, in this particular reaction. On the other hand, a bridged cyclophaneic kind of a system, when it undergoes the photolysis, under this condition, it is only the Dewar Benzene, that is formed, because of the constraint of the bridge, that allows the formation of only the Dewar Benzene. None of the Benzvalene, or the Fulvalene product, can be formed, under this condition.

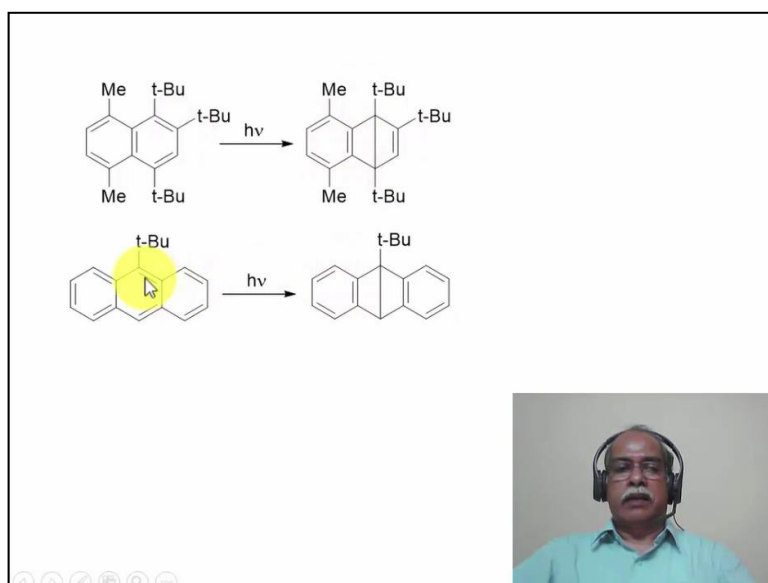
Another example of, Dewar Benzene formation, is a highly-substituted molecule. This is a Hexafluoro Benzene. Hexafluoro Benzene is an electron deficient Benzene system, compared to Benzene itself, because of the electro negative Fluorine, that are attached to it. Nevertheless, it undergoes the UV radiation, nicely to give the Dewar Benzene, as the product. Heavily substituted Benzenes, which are substituted with Tertiary Butyl groups, which are sterically hindered, for example.

This Ortho Di-Tertiary-Butyl group, is sterically hindering each other. So, the molecule is not definitely planar, in this kind of a system. So, in order to relieve the steric hindrance, it undergoes the reaction, to give the Dewar Benzene. In the Dewar Benzene, of course, this two Tertiary Butyl groups, are going to be farther away. This is going to be, in the plane of

the double bond, whereas this is going to be, above the plane of the double bond, for example.

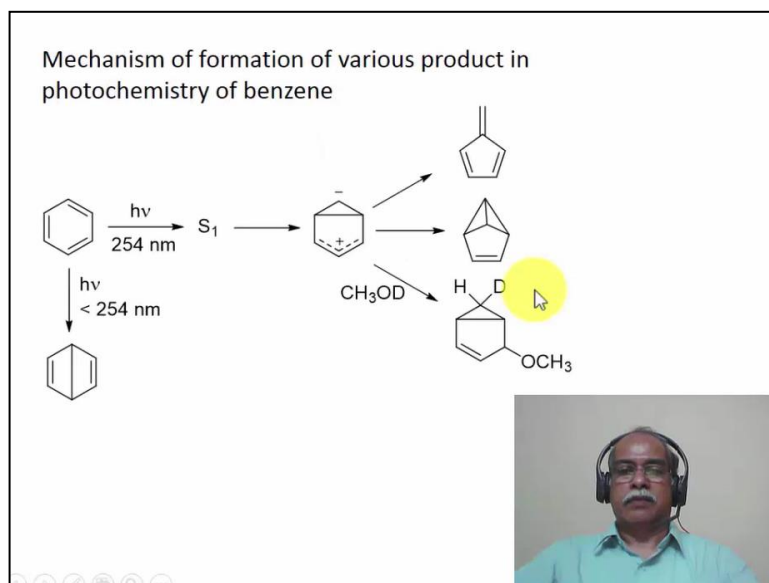
So, these two Tertiary Butyl groups, will move away from each other, during the course of this reaction. This could be, one of the driving force, for this reaction. Benzene itself, undergoes this reaction, only at a very low wavelength. In other words, high-energy radiation is necessary. Whereas, this reaction can be performed, by irradiating the Benzene, around 250 Nanometer itself, indicating that, this could be arising, actually from the S1 state of the Benzene.

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Again, heavily substituted Naphthalene, or Anthracene units, can also undergo the Intramolecular electrocyclization reaction, to give the Dewar Benzene. Here again, Intramolecular electrocyclization reaction, gives the Dewar Benzene, as the final product, in this particular case.

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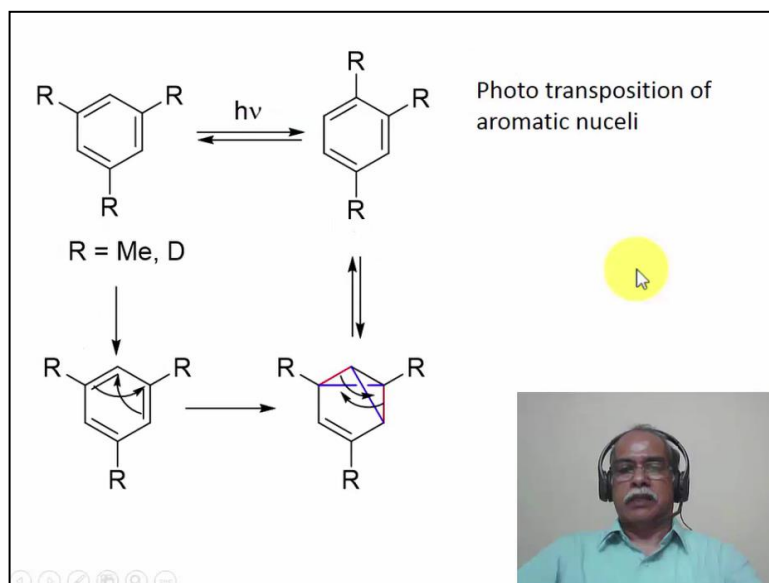


The mechanism of formation, of these various products, that we have seen, in the case of Benzene, is shown here. When it is less than 254 Nanometer, this could be arising out of the S2 excited state of Benzene, giving the Dewar Benzene. If it is arising from the S1 excited state of Benzene, then it can invoke a Dipolar state, of this kind. From the Dipolar state, for example,

One can easily go to the Benzvalene, by connecting this Carbon and this Carbon, with the double bond here, or connecting this Carbon and this Carbon, with the double bond resulting here, essentially forming the Benzvalene. The reason that, it is possibly a Zwitter ionic intermediate is given, by the trapping experiment, when Methanol-D is used, for example, the Methoxy group, essentially goes to the Cationic part, and the Deuteron go to the negative part, in order of producing, this particular molecule.

The Fulvalene can also be explained, by the ring opening of this Cyclopropyl ring, that is shown here, by means of breaking away, that this bond, or this bond, followed by the rearrangement of the PI electron system, to give the Fulvalene, as the final product, in this particular instance.

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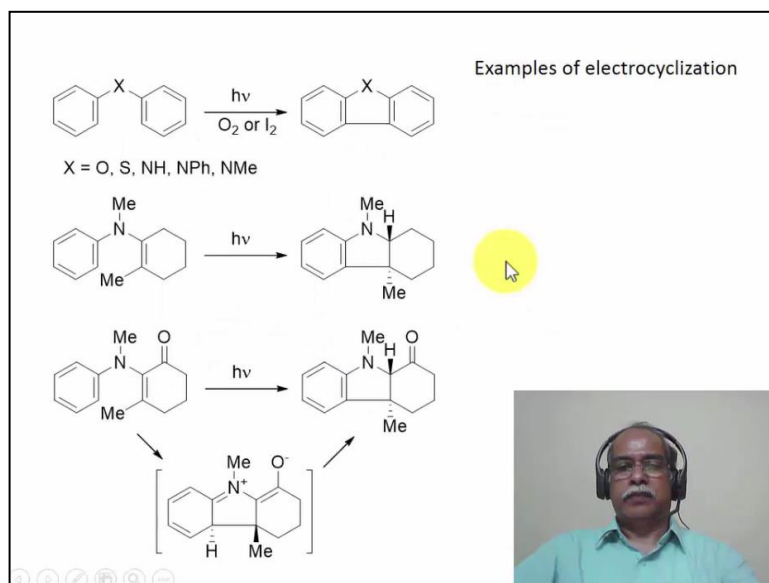


Now, certain substituted Benzene derivative, particularly Mesitylene and 1,3,5-Trideutero-Benzene, when it is photolyzed, they undergo the transposition of the substituents, by scrambling of the substituent, for example. This is easily explained, by the formation of Benzvalene, as an intermediate. The Benzvalene is essentially formed, by the mechanism, that is shown by this arrow.

This is a 1,2-Shift, followed by a 1,2-Shift, resulting in the formation of the, two Blue bonds are formed, during the course of this reaction. And, when you break the molecule, to go to this particular product, the two Red bonds are to be broken. And, that will essentially give the, this is a 1,3,5-Substituted starting material, which gives 1,2,4-Substituted derivative, during the course of photo isomerization, which transpositions the substituents in a different manner, compared to the starting material.

The mechanism, essentially involves an intermediate, which is a Benzvalene intermediate. The Benzvalene intermediate, can reversibly, undergo this particular. Here also, the reversible arrow, should be there. In fact, it can reach a photo dynamic process. In other words, the photo stationery state can be obtained, by this particular reaction. The concentration of the individual species, will depend on, which one is absorbing, and which one is facile, in terms of undergoing this Benzvalene structure, and so on.

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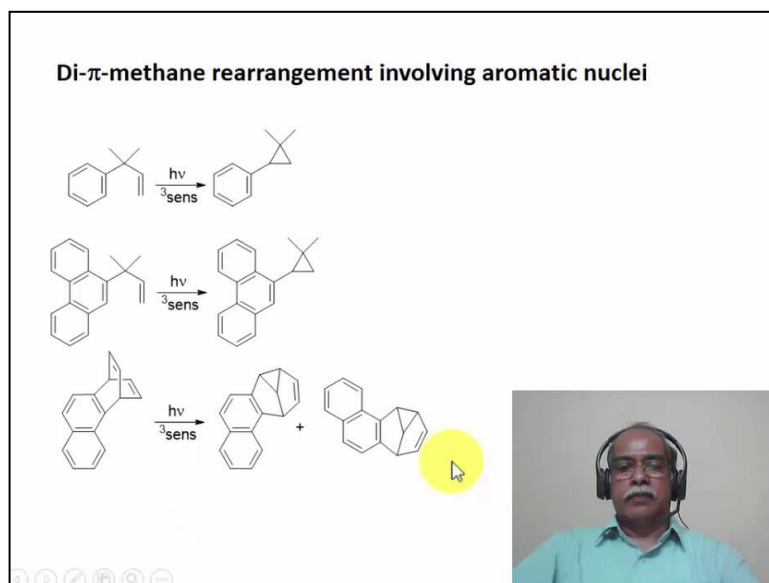
Now, further examples of electrocyclization, involving Heteroatom, in this case, for example. This is Diphenyl Amine, or Diphenyl Ether, or Diphenyl Sulfide, a 6-Electron cyclisation can take place. 6-Electron cyclisation, will form a bond, between these two centers. Why 6-Electron? 2-Electrons from this Benzene, 2-Electron from this Benzene, and a lone pair of electron, from the Heteroatom.

So, overall, it is a 6-Electron system. Under Photochemical condition, it is a Conrotatory process, resulting in the formation of a Dihydro Aromatic derivative, which is oxidized by either Iodine or Oxygen, to give the fully Aromatic. This can give, Dibenzofuran, Dibenzothiophene, Or Diphenyl pyrrole, for example, as the case may be. Diphenyl pyrrole, is essentially, when X is equal to NH, that will be Diphenyl pyrrole.

Now, this molecule, essentially is undergoing electrocyclization reaction, followed by a Hydrogen transfer to this position, leading to the formation of this Trans stereochemistry, in this particular junction. The mechanism is, when the Alpha Beta Unsaturated Ketone is part of the ring system, mechanism involves a Zwitter ionic species, here. This is essentially, an electrocyclization. Electrocylation, followed by a Proton transfer, to give this particular product.

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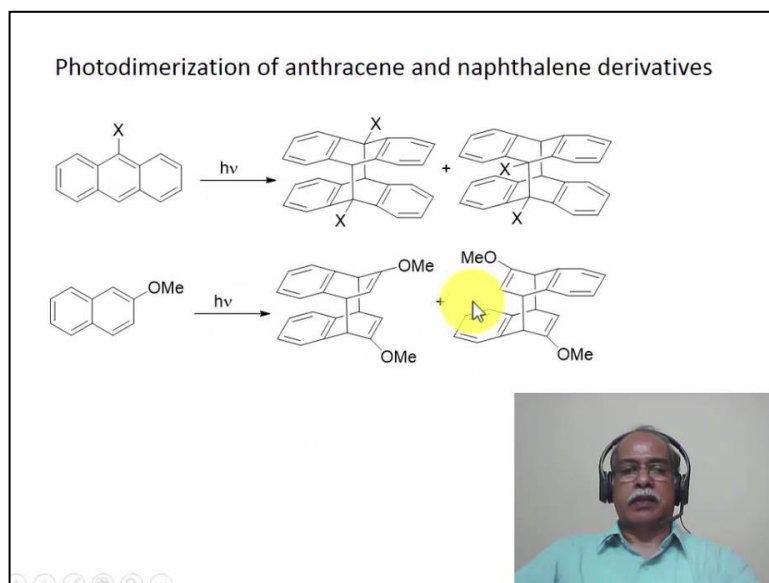




The Di-PI-Methane rearrangement, is possible. We have already seen this, in the Di-PI-Methane system. Let me, recap it. Di-PI-Methane rearrangement, is nothing but, 1\_2\_3\_4, 1,4-Pentadiene kind of a derivatives, where 1,4-Pentadiene is part of an Aromatic system, resulting in the formation of a Cyclopropyl Phenyl derivative, in the Di-PI-Methane rearrangement. In other words, it is a 1,2-Shift, is what we are talking about, in terms of the rearrangement process.

This is essentially happening, in the presence of a sensitizer. That means, it will undergo this reaction, through a Triplet state intermediate, is what is formed, in this particular case. So, all this case, essentially correspond to the, Di-PI-Methane rearranged product. Here, Di-PI-Methane rearrangement can give, potentially two products. The double bond can be, either here, or here, in the canonical structure. So, the two types of products, that are indicated are, even in this particular structure of the product, that are shown here.

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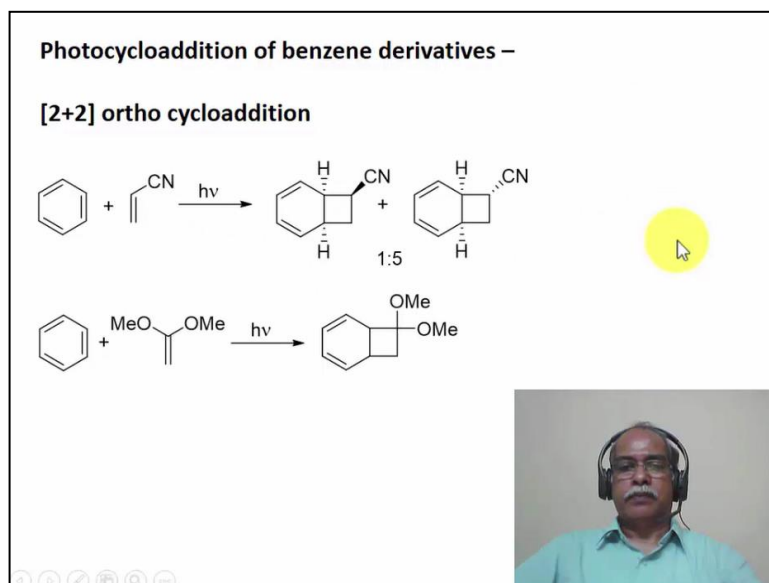


Now, Photodimerization of Anthracene is something, we have dealt with, in the Pericyclic reaction. Photodimerization of Anthracene, essentially involves the, 9\_10\_Position of Anthracene, resulting in the formation of photodimers. This is a, Head-to-Tail dimer. And, this is a, Head-to-Head dimer. Depending upon, the orientation of the two Anthracene unit, one can either form the, Head-to-Head, or Head-to-Tail. In fact, both the compounds are formed as a mixture, in most of the Photochemical Cycloaddition of Anthracene.

Naphthalene can also undergo, the 4PI-4PI-Cycloaddition reaction. Essentially, it can either overlap on top of other, or it can overlap, by sliding itself into the other ring, sliding out of the plane of the Methoxy ring, resulting in the formation of two types of products. Both the products are essentially, 4PI-4PI-Cycloaddition product, which could be a concerted process, arising out of the funnel mechanism. In other words, this is probably, no intermediate is involved.

The first excited Singlet state essentially, directly undergoes reaction with the ground state Anthracene, to produce this molecule, through a funnel mechanism, which is essentially a Frank-Condon transition, is what is taking place, during the course of this reaction.

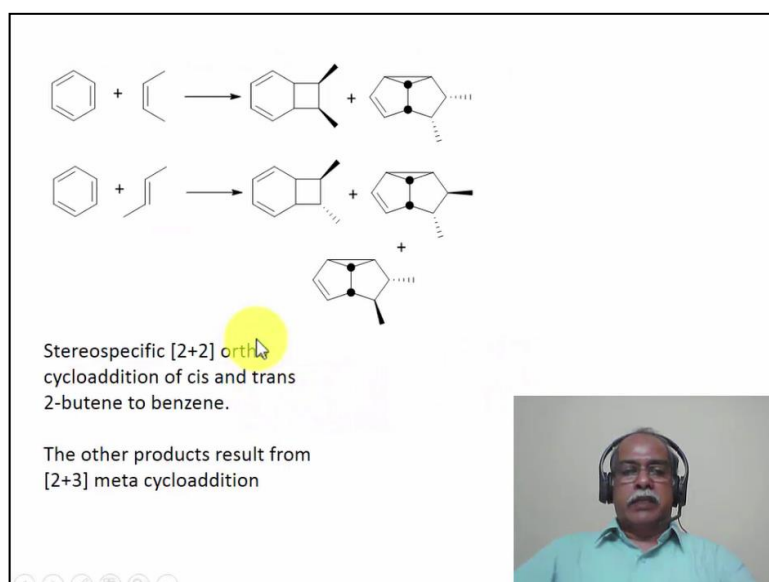
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Benzene, does not undergo Diels-Alder reaction, except with Dicyano Acetylene. With Acrylonitrile, or electron-rich, or electron-deficient Olefins, it undergoes 2+2-Cycloaddition reaction, which could be considered as a concerted reaction. The 2+2-Cycloaddition reaction essentially, is a stereoselective reaction, in the formation of this particular product, in 5:1 ratio, is what is the diastereomeric products are, arising out of 2+2-Ortho cycloaddition.

Here, electron rich Olefin, also undergoes 2+2-Cycloaddition reaction, to give the corresponding Cyclohexadiene, fused with the Cyclobutane as the ring system, that we have in the product stage.

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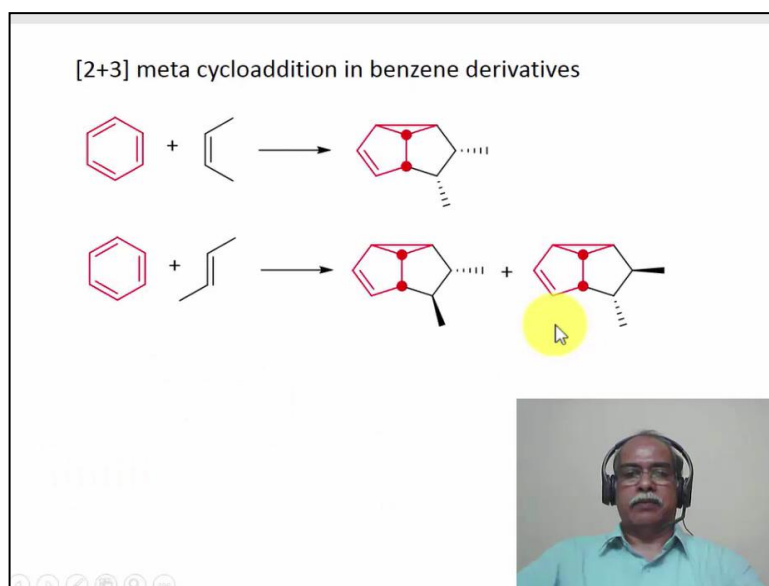


The reaction has been shown, to be stereo specific, when Cis and Trans isomers of 2-Butene, are used. When the Cis isomer of 2-Butene is photolyzed, along with the Benzene, the

corresponding 2+2-Cycloaddition reaction product is formed, with the two Methyl groups, which are Cis, with respect to each other.

So, essentially, it is a highly stereospecific reaction. When the Trans-isomer is used, the Cyclobutene, with the two Methyl groups are formed, with the Trans stereochemistry, with respect to each other. These three products, which are arising out of 2+3-Meta-Cycloaddition product, we will discuss it, in the next slide.

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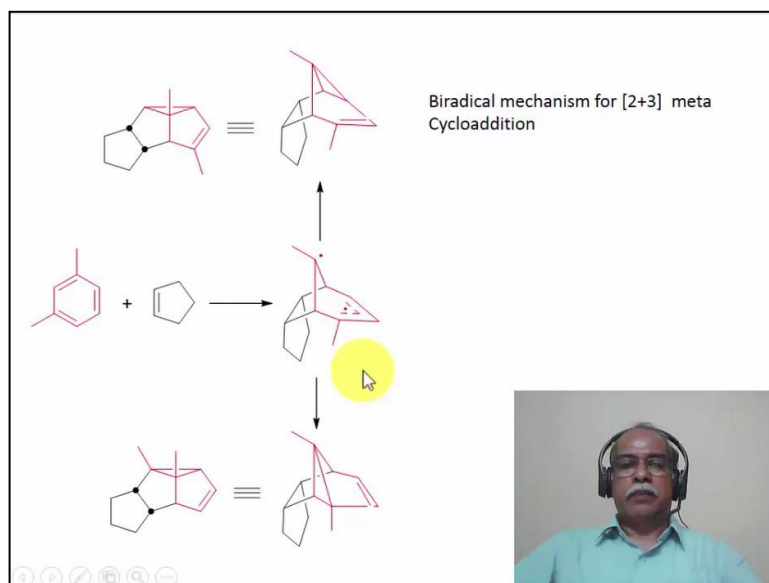
Now, in the case of the, these three products, which are separately written here, with the Cis-2-Butene, and Trans-2-Butene, the two products are formed.

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If you trace out, the Red portion of the molecule here, you will see Benzene. In other words, this is 1\_2\_3\_4\_5\_6 though, this corresponds to a Benzene ring. Obviously, the addition has undergone 2\_3. In other words, the 1,3 position of Benzene, has undergone Cycloaddition reaction, with the Olefin.

So, overall if you look at, it is looking like a 2\_3, 3-Carbons of the Benzene, and 2-Carbons of the Olefin, are undergoing the Cycloaddition reaction, with the concomitant rearrangement of the PI system, to give this particular product.

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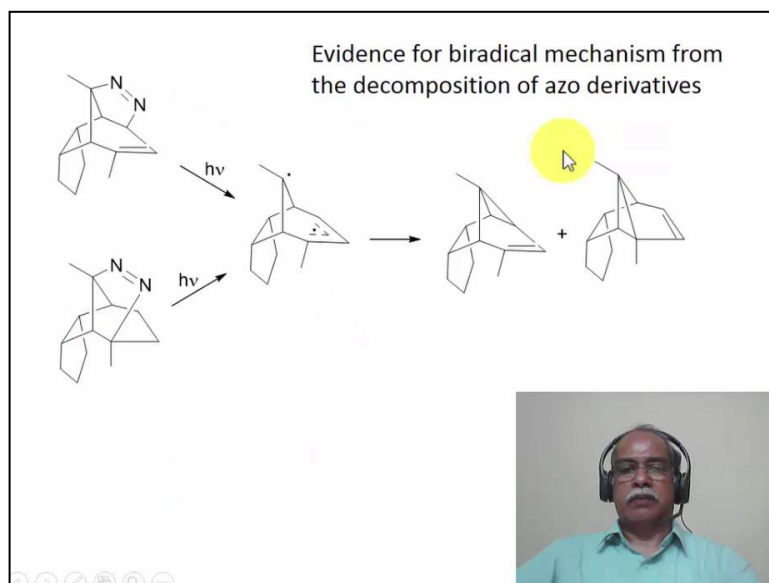


the mechanism, can be explained as follows, with Cyclopentene as, illustrating the example. Cyclopentene, undergoes 2,3-Cycloaddition process, to give a Diradical intermediate, of this type. The Diradical, can either close from, here to here, or, it can close from, here to here. These are the two processes, that can be shown. And, obviously, the two products that are formed are, this product, and this product.

These two structures, are identical structures. If you want, you can number the structures, and follow the numbering, to arrive at the structure. So, essentially this structure is formed by, 1,3-Ring closure, of these two radical centers. 1,3-Ring closure, of these two radical centers, will essentially form this particular product, in this particular case.

So, the formation of these three products, can be explained on the basis of the, 2+3-Meta-Cycloaddition process. It is a very interesting reaction. You can see here, it is a highly-strained molecule, a tricyclic molecule, is easily produced, from Benzene, by photolysis with the, simple Olefinic kind of a system.

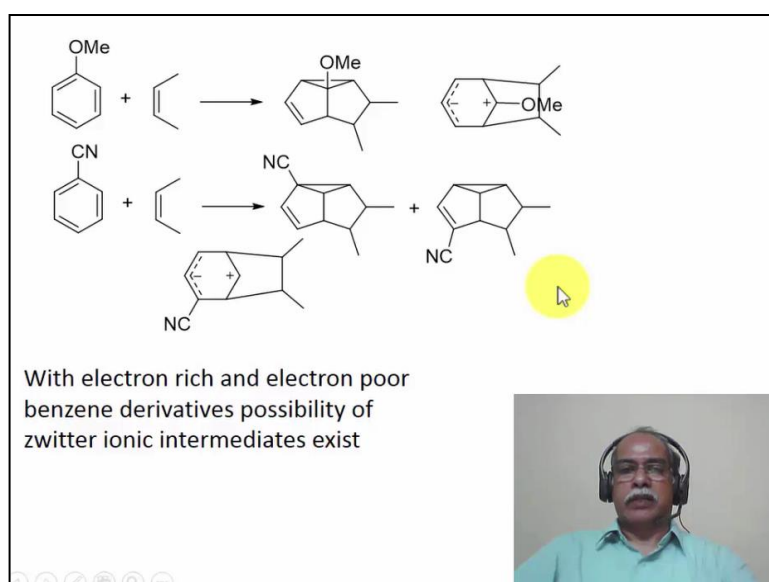
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Now, the fact that, we are invoking a Diradical intermediate, needs proof, as far as the mechanistic detail is concerned. When the Azo compound of this kind, is decomposed, either this Azo compound, or this Azo compound, is decomposed, it forms a Diradical intermediate. The Azo compound decomposition, also gives the same product, as the Benzene Cycloaddition product.

These three compounds, that are formed here, can essentially come from the, decomposition of the Azo compounds also, indicating that the, Diradical intermediate is a true picture of the, mechanism of this particular reaction, of 2+3-Cycloaddition process.

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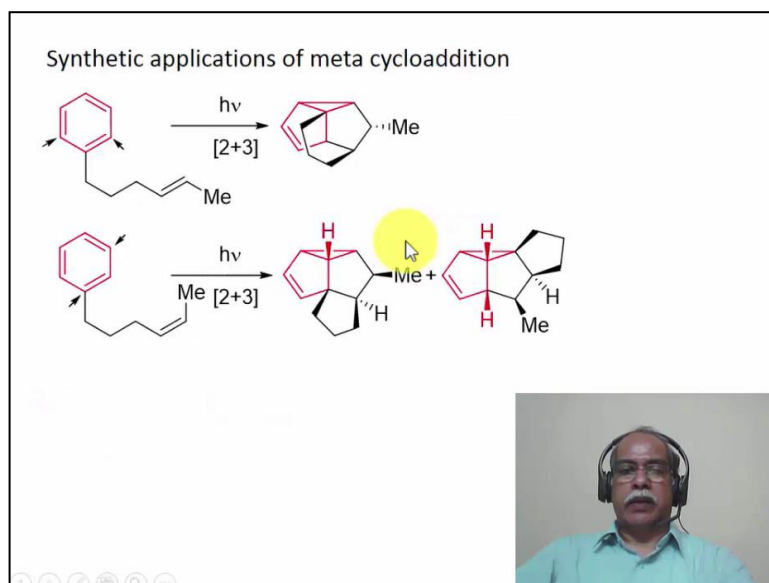
When highly polar substituents are there, either electron donating substituent, or electron withdrawing substituent, it is possible that, this reaction goes through a dipolar intermediate. The dipolar intermediate, is shown here, for example. 2+3-Cycloaddition reaction of

Benzene, in the case of the Methoxy substituted derivative, will have this particular system. Now, this can undergo ring closure, between these two Carbons, or between these two Carbons, essentially forming this particular product.

In the case of, electron withdrawing substituted derivative, the negative charge, stays with the Cyano functional group. Again, the bond formation, between these two centers, to produce this particular Cis product. Between, these two centers, will produce the other product, which is this particular product, for example. So, one can invoke the formation of the, Zwitter ionic intermediate of this type, in a 2+3-Cycloaddition process, particularly with the electron rich, as well as electron poor, Benzene derivative.

The possibility of this intermediates, do exist, which can be explained, by the stabilization of the charges, by the electron donating, and electron withdrawing substituents, in these systems. So, without any electronically biasing substituent, it can go through a Diradical intermediate of this type, with strongly electron influencing systems, like the electron donating, or electron withdrawing substituent, it could be a Zwitter ionic intermediate, of this type.

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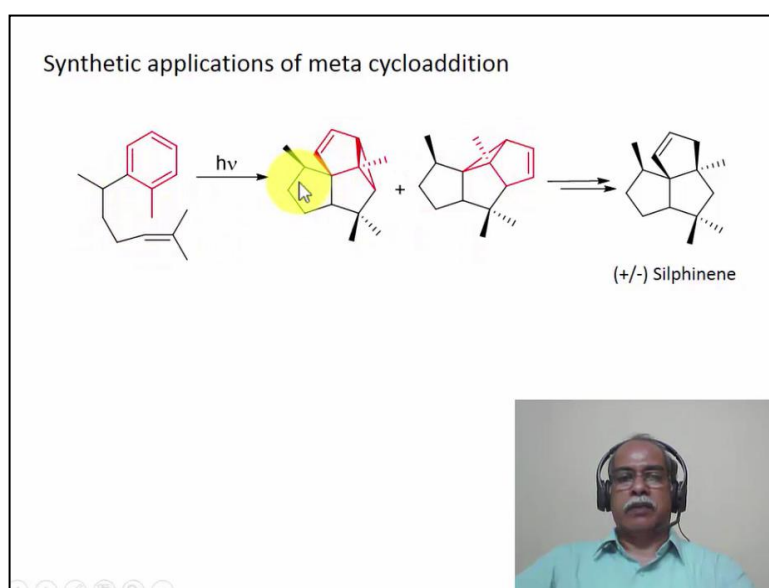
Synthetic applications of the Metacyclic cycloaddition, is what is given here, beautifully. These are, intramolecular versions of the, Cycloaddition reaction. So, it gives a fairly complex, Tetracyclic compound, of this type. Essentially, the Cycloaddition reaction takes place, between the 1,3-Positions, which are indicated by arrow, across this double bond, resulting in the formation of the structure.

So, if you follow the Black portion of the substituent, essentially that will give you the pendant group. The Red portion, essentially indicates the Benzene ring itself, which has

undergone substantial reorganization, in terms of the Meta-Cycloaddition process. Again, you will see that, the Meta-Cycloaddition process, is a highly stereo selective process. The stereochemistry of the double bond, is essentially retained, in the product also.

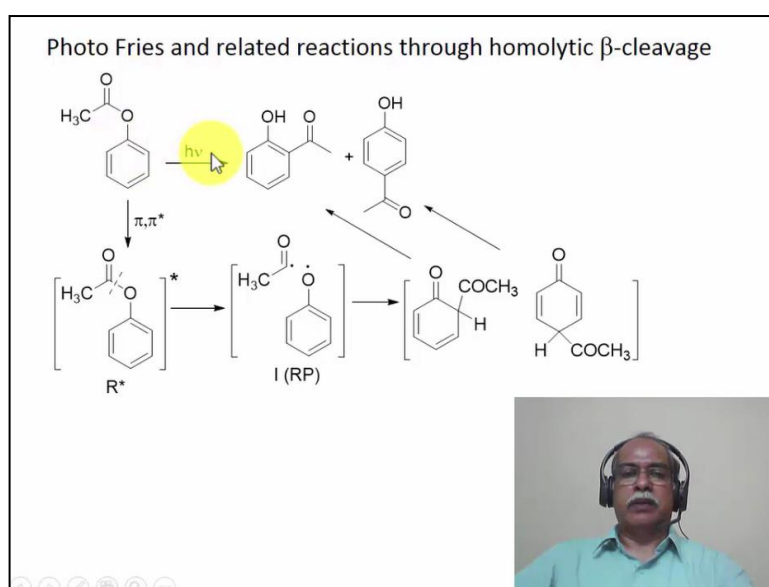
As you can see, in the stereochemistry, this is Hydrogen, and Methyl, are trans. You can see, Hydrogen and Methyl, are trans. Here, the Hydrogen and Methyl, are Cis. Again, the Hydrogen and Methyl, are Cis, in this particular product of, Cycloaddition product, that is shown here.

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The synthetic application of Meta-Cycloaddition, is further illustrated by the, addition of this pendant group, which is attached to the Benzene ring, in terms of forming the Angularly fused system, as well as Linearly fused system. The Angularly fused system, is further transformed into a Terpenoid molecule, namely Silphinene, is the Terpenoid molecule.

Racemic synthesis of the Silphinene, is essentially made from this, angularly fused 2+3-Cycloaddition product, of this pendant group, to the Benzene unit, which can be traced by the color-coded ring system, that are. Again, this is part of the, originally the Benzene ring. This is also, part of the original Benzene ring. The substituent, which is this one, is given in the



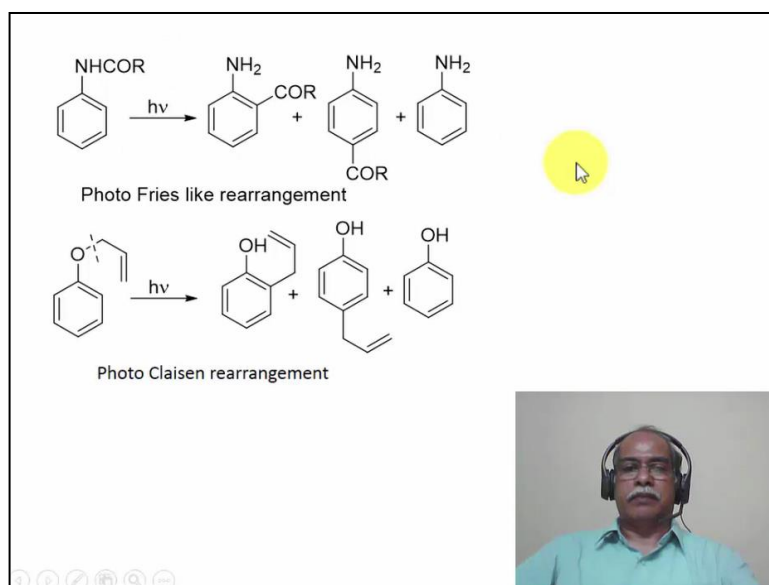


Black portion. So, one can easily trace out the Cycloaddition process, as 2,3-Cycloaddition process.

Let us look at, some Beta cleavage processes, which are homolytic cleavages. If you take for example, Phenyl Acetate, which is a starting material. When you fertilize, the PI-PI-Star excited state of the Phenyl Acetate, essentially weakens the Beta bond, which is this particular bond. This is Alpha bond, and this is Beta bond, producing Acetyl radical, and Phenoxy radical. The Acetyl radical, recombines in the Para position, as well as in the Ortho position, resulting in the formation of the corresponding, intermediate Diradical stage.

The intermediate Diradical recombination, in the Ortho and Para position, will give this intermediate, which is undergoing Enolization, to give the Phenolic product, which is the Ortho Hydroxy Acetophenone, and Para Hydroxy Acetophenone, as the product. This reaction is known as the, Photo-Freeze rearrangement. Because, it resembles the Freeze rearrangement, which is triggered by Lewis acid catalyzed rearrangement of the Phenyl Acetate, for example, to give the same class of products, that is shown here.

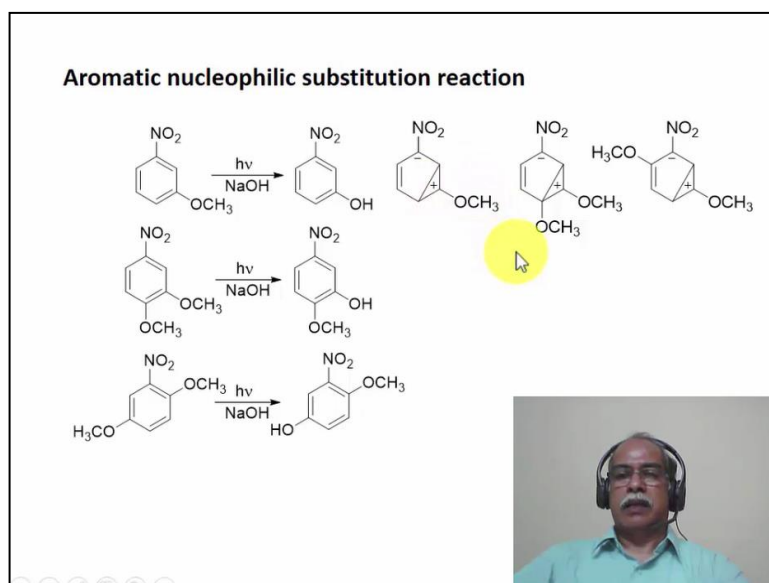
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These are, Photo-Fries like rearrangement. The corresponding Amino derivative, which is the Acetanilide for example, on photolysis gives you, Ortho Amino Acetophenone, and Para Amino Acetophenone, and a small amount of Aniline is formed, because of the leakage of the Acetyl radical, from the reaction medium.

This is another example, which is Photo-Claisen rearrangement. Essentially, an Allyl radical, and Phenoxy radical, is produced. The Allyl radical, combines in the Ortho and Para positions, to give the Ortho Allyl Phenol, and Para Allyl Phenol. Phenol is also a byproduct, that is formed, in this particular reaction.

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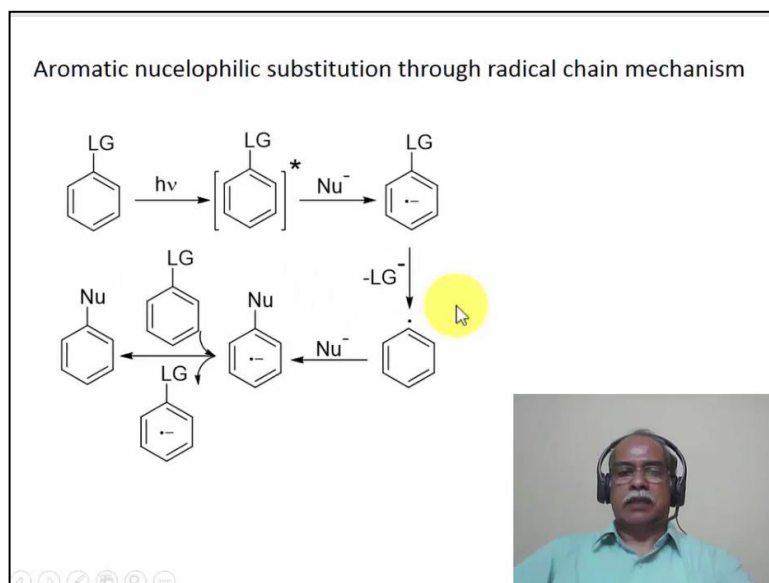
Now, let us move onto nucleophilic Aromatic substitutions, by Photochemical reaction. These reactions, are normally not possible, under thermal condition. For example, if you take, Meta Methoxy Nitrobenzene, and treat it with Sodium Hydroxide, under thermal condition, no reaction can be observed. However, under Photochemical condition, the substitution of the Methoxy group, which is normally, not a good leaving group, takes place, producing the Meta Nitrophenol, for example.

Similarly, if you take 3,4-Dimethoxynitrobenzene, it is specifically the Meta, with respect to the Nitro, that Methoxy alone is substituted. If you similarly, take the 2,5-Dimethoxy Nitrobenzene, it is the Meta Methoxy, with respect to the Nitro, is specifically substituted. So, the reactions are highly regio specific in nature. Atleast, these two examples seem to tell us that, the group that is Meta to the Nitro group, is what is substituted.

So, it is highly regio specific in nature, which can be explained, on the basis of formation of this kind of an intermediate. Remember, the Zwitter ionic intermediate is the, S<sub>1</sub>-PI-PI-Star state is the Zwitter ionic intermediate. In fact, we are doing an S<sub>1</sub> PI-PI-Star excitation, of this Aromatic unit, is what we are doing here. Once, the Zwitter ionic intermediate is formed, it is easy to see, why the Nucleophile will attack, in this position. Because, it is an electron deficient position.

The Anionic charge is stabilized, by the Nitro functional group, whereas the Cationic charge is stabilized, by the Methoxy functional group. So, Nucleophile can essentially attack this position, with the Methoxy as the leaving group, for example, which would explain, the formation of the products, that are shown here.

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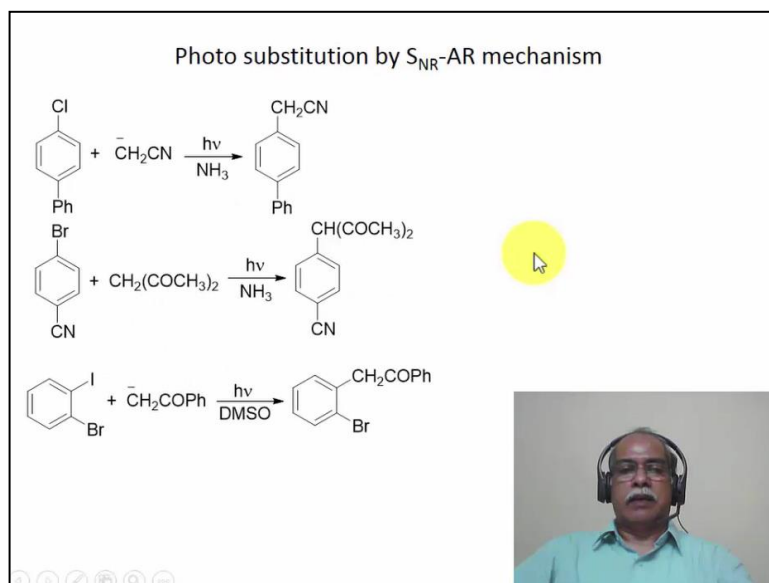


Alternatively, if you have a good leaving group, which is a Halogen as a leaving group, for example. And, we have a very powerful Nucleophile, which are Carbon Nucleophile. One can also have a mechanism, passing through a, radical chain mechanism. Let me explain, this mechanism. Initially, the Benzene ring is substituted, with the leaving group, which could be a Halogen like Chlorine, or Bromine, or Iodine. Upon photolysis, it goes to the Singlet excited PI-PI-Star state.

And, under these condition, a powerful Nucleophile like a Carbon Nucleophile, can undergo electron transfer processes, to the excited state molecule, resulting in the formation of an Anion radical, and the Nucleophile radical also, will be produced in the process. In other words, there is an electron transfer on the Nucleophile, to the excited state of the Benzene ring, producing the Anion radical of the Benzene ring, itself. Now, this is a fragmentative process. Once the Anion radical, with the Chlorobenzene Anion radical is formed, the Carbon Chlorine bond, can be easily cleaved.

Chloride can leave, for example, producing a Phenyl radical. The Phenyl radical can be trapped, by the Nucleophile, to give another radical Anion species, which is a chain propagator for example. Now, the starting material can be reduced, in the reduction potential of this, should be lower than the, reduction potential of this. So, electron transfer can take place, between these two, producing these, chain propagator, and the Nucleophile substituted molecule.

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This examples of, this kind of reaction, is illustrated here. Typically, these reactions are carried out, in a very Polar solvent like Ammonia, or a DMSO, and so on, where the Anions can be easily generated. In this particular instance, for example, Acetonitrile Anion, which can be generated from, Acetonitrile in Ammonia, or in LDA, as the base, for example. The Para Phenyl substituted, 4-Chlorobiphenyl for example, undergoes substitution by this Carbon, to give the corresponding,  $\text{CH}_2\text{CN}$  substituted product.

In this case, this is, Acetyl Acetone is the molecule. Acetyl Acetone, can produce the corresponding Carbanion, in the presence of Ammonia. And, the Carbanion essentially undergoes, the substitution of the Bromine, via this radical Anion mechanism, through electron transfer process.

So, these are called, substitution, nucleophilic, radical, Aromatic, Aromatic substitution reaction, is what we are talking about. Radical mechanism, is what we are implying, in this particular case. In this case, there is a selectivity between, Bromine and Iodine. Iodine is specifically substituted by, Acetophenone Anion, for example, to give the corresponding Benzyl Phenyl Ketone, as the final product, in this case.

What we have seen, is a glimpse of the Photochemistry of Aromatic molecule, which are rich in PI-PI-Star excited state process. The models for the PI-PI-Star excited state, depends on, whether we are dealing with the first excited state Singlet, or first Triplet excited state of the molecule.

The first excited Singlet state, is typically a Zwitter ionic kind of an intermediate. Whereas, the first Triplet state, is a Biradical kind of an intermediate. The various reactions, arising out of the Benzene, transforming into 2+2-Cycloaddition reaction, or 2+3-Cycloaddition reaction, or substitution reaction, can be explained, by invoking the Zwitter ionic

intermediate, or the Diradical intermediate, kind of a model systems, that we discussed. I hope, you enjoyed this module. Thank you very much, for your kind attention.