Pericyclic Reactions and Organic Photochemistry
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Module No. #07
Lecture No. #30
Photochemistry of Carbonyl compounds: Norrish Type 1 and 2 reactions

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Hello, welcome to the online course on, Pericyclic Reactions and Organic Photochemistry. We will continue with, Photochemistry of Carbonyl compounds, in Module Thirty. Carbonyl compounds exhibit, two important types of Photochemical reactions, called Norrish Type One, and Type Two reaction. We will consider, both these types, in this particular module.

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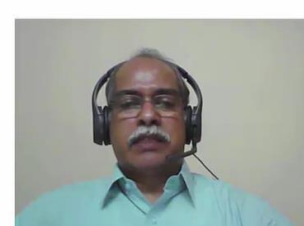Photochemistry of carbonyl compounds is dominated by n,π* excited state

Most carbonyl compounds have efficient ISC and hence the reactions occur from the ^{1}T (n,π*)

Reactivity of ^{1}T (n,π*) can be compared to that of alkoxy radicals

alkoxy radical model for n-π* state

Hydrogen abstraction
Addition to C=C
Cleavage of α-bond

Now, if we consider the Photochemistry of Carbonyl compounds, it is dominated by the N-PI-Star excited state. Remember, the N-PI-Star excited state, is the lowest energy transition state, in most of the Carbonyl compounds. So, most Carbonyl compounds, also have a very efficient Intersystem crossing. ISC is Intersystem crossing, that is converting from the Singlet excited state, to the Triplet excited state.

Hence, most of the reactions occur, from the N-PI-Star state, which is also a Triplet state, in the case of Carbonyl compounds. The reactivity of the Triplet N-PI-Star state, can be compared with Alkoxy radical. You consider this, to be the excited Carbonyl compound. From the electronic configuration point of view, one can represent, this as the Diradical kind of an intermediate. This Diradical represents the excited state of the, N-PI-Star state of the, Carbonyl compound.

If you look at the structure of Alkoxy radical, there is a similarity, in terms of the electronic structure, except this Carbon radical is missing, instead you have a Tetravalent Carbon, in this particular case. Alkoxy radical, serves as a model, for the N-PI-Star state of Carbonyl compounds. How do they do that? For example, Alkoxy radicals are capable of undergoing, Hydrogen abstraction reaction.

Excited state Carbonyl compounds, also undergo Hydrogen abstraction reaction, provided, a suitable Hydrogen is available, which can be transferred onto the Oxygen of the excited state Carbonyl functional group. They can add to, Carbon-Carbon double bond. They can also undergo, cleavage of the Alpha bond. Alpha bond meaning, this particular bond, which is adjacent to the Carbon radical center, that is here, for example. So, let us have a look at, some of the reactions, in the due course.
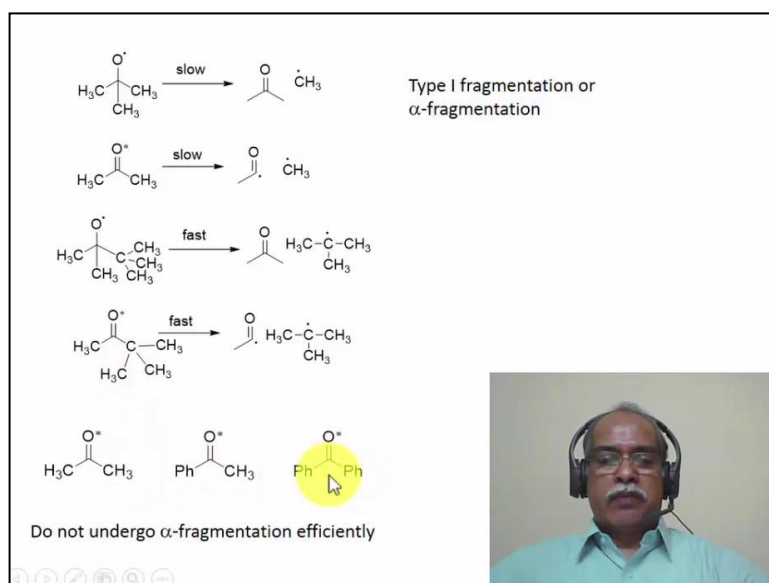
Now, this essentially demonstrates the analogy, that is drawn between the Alkoxy radical, and the fragmentation process, that it can undergo. The Alpha fragmentation, is what is represented, by this equation. If you take a Tertiary Butyl radical, it can undergo fragmentation, to give a Methyl radical, and Acetone. However, Methyl radical is not a stable radical. So, the energy for this particular fragmentation, will be very high. As a result, this is not a very efficient process.

So is the Acetone excited state, which is now serving as the, analogy to the Tertiary Butyl radical. Acetone, in the excited state, it does not undergo Alpha fragmentation very efficiently, for the simple reason, the Methyl radical that is produced, is not a very stable radical. On the other hand, if we take Tertiary Butyl Dimethyl Methyl Oxy Radical, which is this particular radical here, this Alkoxy radical, readily loses Tertiary Butyl radical, producing Acetone, and Tertiary Butyl radical.

Tertiary Butyl radical, being a stable radical, it is a tertiary radical. So, it is a relatively speaking, more stable than a Methyl radical. This fragmentation process is very fast, compared to this low fragmentation process, of the Tertiary Butyl radical, itself. Similarly, if you take Tertiary Butyl Methyl Ketone, in the excited state, it undergoes the Alpha fragmentation quite readily. In fact, this fragmentation is very fast, compared to the fragmentation of Acetone itself.

So, this produces essentially an Acetyl radical, and a Tertiary Butyl radical. So, this kind of a reactivity pattern, is what suggest to us that, an Alkoxy radical can be a model for the, N-PI-Star excited state Carbonyl compounds, for example. Those Ketones, which do not produce a

stable Alkyl radical, for example, Acetone, Acetophenone, Benzophenone, they do not undergo, Alpha fragmentation efficiently, from the excited N-PI-Star state.

Because, this will produce, either a Phenyl radical, or a Methyl radical, both of which are unstable. This will produce Phenyl radical, which is also unstable. Relatively speaking for example, compared to a Tertiary Butyl radical, these radicals that are produced by Alpha fragmentation, from these excited state Ketones, are quite unstable. So, they are not produced. Therefore, these Ketones do not undergo fragmentation, very efficiently.

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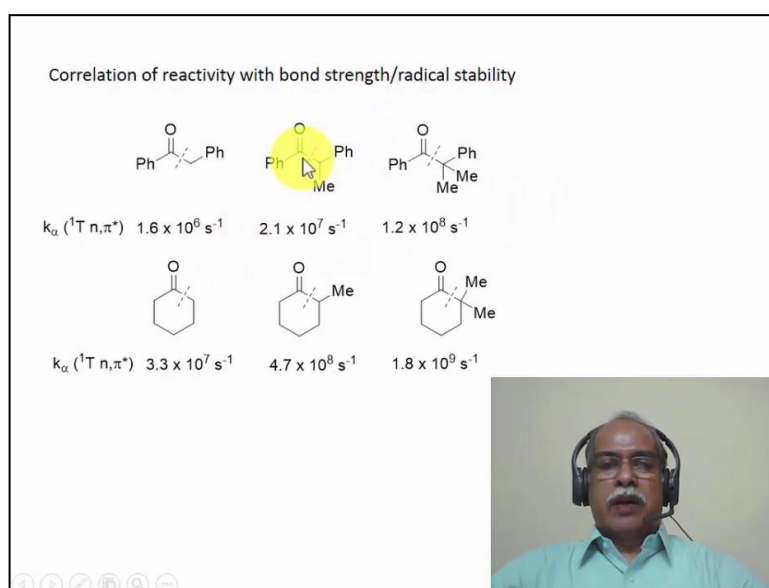
This shows, the relative bond strength, and the radical stability, towards the rate of the Alpha fragmentation. The dash line shows that, this is Alpha bond, that is undergoing the fragmentation. That is a reaction, that we are considering, in this particular slide. The K-Alpha is the rate of fragmentation, from the N-PI-Star Excited Triplet state, of this Ketones. In other words, photo excited state of these Ketones, correspond to N-PI-Star Triplet state. And, these are the rates constants, for the cleavage of the Alpha bond, to produce a corresponding radical.

As you go from the, Benzyl Phenyl Ketone, to the Phenyl Methyl Benzyl Ketone, or the Dimethyl Phenyl Methyl Phenyl Benzyl Ketone, for example. These three Ketones, if you take, the Alpha fragmentation, produces a Diphenyl Methyl radical, in this particular case. Whereas, this gives a Phenyl Ethyl radical, which is a secondary radical. This is a tertiary radical. So, as you go from the left-hand side Ketone, to the right-hand side Ketone, the fragmentation produces, more and more stable radicals.

This is reflected, in the rate of the reaction being increasing, by two orders of magnitude. From 1.6×10^6 per second, it goes to 1.2×10^8 per second, which is two orders of magnitude

difference, between the rate constants of the fragmentation process, that is shown here. If you take the Cyclohexanone series for example, cyclic Ketone series, simple Cyclohexanone, does not undergo fragmentation, quite readily.

Whereas, Alpha Methyl substituted one, is faster by an order of magnitude. Alpha Dimethyl substituted one, undergoes even faster, by an order of magnitude, compared to the Alpha Methyl one. The reason being, this produces a primary radical, this produces a secondary radical. Whereas, this produces a tertiary radical, which is a stable radical. So, this essentially illustrates that, the more and more substituents that you have in the Alpha position, the Alpha bond becomes weaker, in the excited state.

In fact, the Carbonyl bond gets stretched out, lengthened, which in turn weakens the Carbon-Carbon bond, which is an Alpha bond. And, in addition to that, if the radical produced is also stable, then that particular fragmentation process, is a favorable process. That is all, this particular slide is illustrating, in terms of the rate of reactions being observed, with respect to the strength of the Alpha bond, and the stability of the resulting radical, that is produced.

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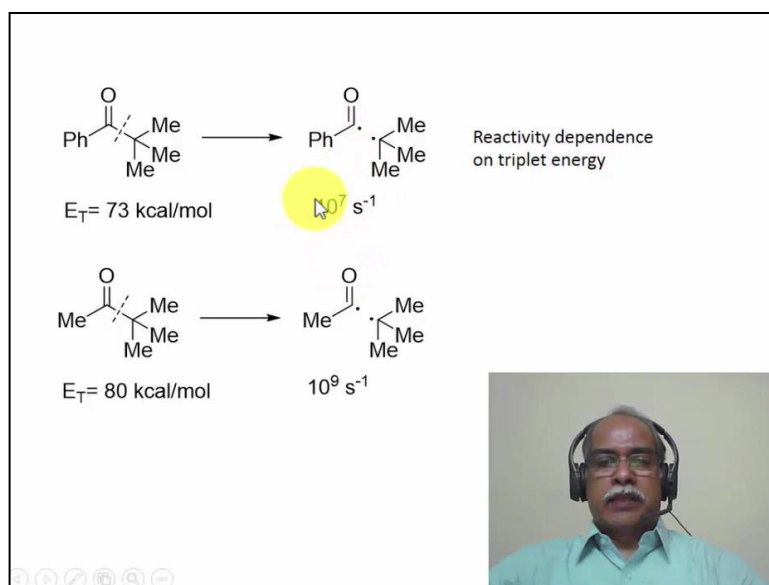
Now, the fragmentation rate also, depends on the, electronically excited state. How, far away, it is from the grounds electronic state, for example. If you look at the, Triplet energy state of this Tertiary Butyl Phenyl Ketone, it is about 73 Kilocalories per Mole. Whereas, if you take the Triplet state of the Tertiary Butyl Methyl Ketone, it is about 80 Kilocalories per Mole. So, about 7 Kilocalories up higher in energy, this particular one. So, the higher the energy, the bond fragmentation becomes faster.

This is undergoing a fragmentation process, by two orders of magnitude, compared to this particular fragmentation process. The 10^7 and 10^9 per second, are actually the rates of the

Alpha fragmentation process. So, this clearly illustrates, the reactivity depends on the Triplet energy of the Ketone, that is associated with the fragmentation process.

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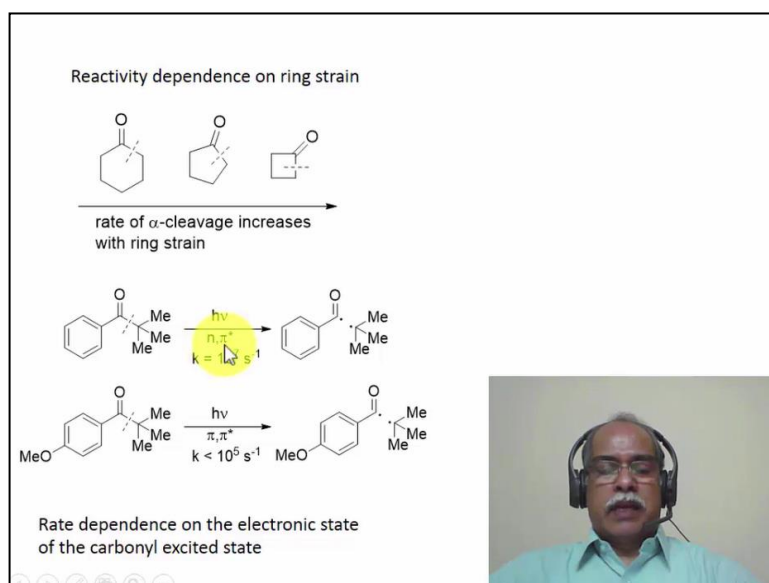
Now, the ring strain can also play a role, in the fragmentation rate. The more the strain, the ring has, the faster will be the fragmentation. A 6-Membered ring is relatively, strain free molecule. Compared to that, 5-Membered ring is, somewhat more strained. 4-Membered ring is, definitely strained. So, as you go from the Cyclohexanone Pentanone, to the Cyclobutanone, the Alpha fragmentation process, identicated by the dashed lines here, which represents Alpha bond breakage.

As the strain increases, the rate of cleavage of the bond also increases, with the ring strain. Now, the excited state also matters, whether it is a N-PI-Star state, or the PI-PI-Star state. Some of the Ketones, for example, the Para Methoxy Phenyl Tertiary Butyl Ketone, or the Para Dimethyl Amino Phenyl Tertiary Butyl Ketones, they have the lowest energy state, to be a PI-PI-Star state, and not an N-PI-Star state.

In fact, for this Ketone, the N-PI-Star state, is higher than the PI-PI-Star state. So, the reaction specifically occurs from the PI-PI-Star state, because that is the most easily accessible state, which is a lower energy state, compared to a N-PI-Star excited state. So, if it has an N-PI-Star excited state, the fragmentation process is much faster, because of the Triplet state, associated with the N-PI-Star state.

On the other hand, if you have a PI-PI-Star state, that does not have the, same kind of a reactivity, you can see here, it is about two orders of magnitude less, in terms of the fragmentation reaction rate, compared to the one, that is coming from the N-PI-Star state. So,

the rate dependence, on the electronic state of the Carbonyl excited state, is illustrated by this two example.

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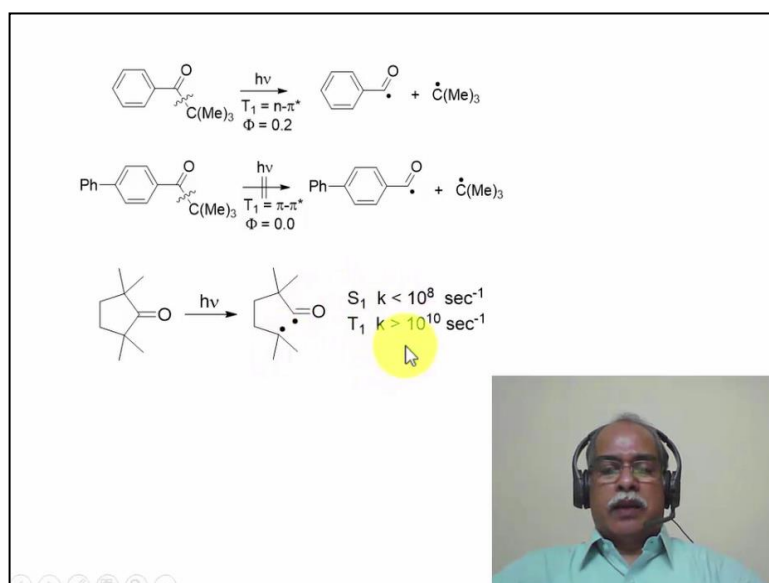
Two more examples, also shown here. This, Bi Phenyl Tertiary Butyl Ketone, does not undergo, any fragmentation process, at all. Because, it's Triplet state, it is a PI-PI-Star state. Whereas, in the case of Tertiary Butyl Phenyl Ketone, the Triplet state is an N-PI-Star state, with a Quantum efficiency of about, 0.2 for the fragmentation process. This has a Quantum efficiency of zero. That means, no fragmentation will be observed. In spite of the fact that, you are producing a, likely to produce a Tertiary Butyl radical, because the PI-PI-Star state, does not weaken the Alpha bond.

So, as a result of that, compared to the N-PI-Star state, the PI-PI-Star state is extremely unreactive, towards Alpha fragmentation process. It may undergo, several other different types of reaction, a PI-PI-Star state can undergo. But, N-PI-Star state is the specific state, from which the Alpha fragmentation takes place. So, that does not take place, if the lowest energy state, is a PI-PI-Star state. Now, here again, the same principle is illustrated.

When this Ketone is fertilized directly, it has an accessible Singlet state, which is fragmentation process is about 10^8 second. If you do a sensitized transfer of energy, to a Triplet excited state, then it has a two orders of magnitude rate constant, higher than the Singlet state, for example, clearly illustrating, the electronic state matters, in terms of the N-PI-Star Triplet state, being much more favorable for the Alpha fragmentation, compared to a Singlet state, which can be a N-PI-Star state, for example.

The spin multiplicity makes a difference, in terms of a fragmentation process, that takes place, in this case.
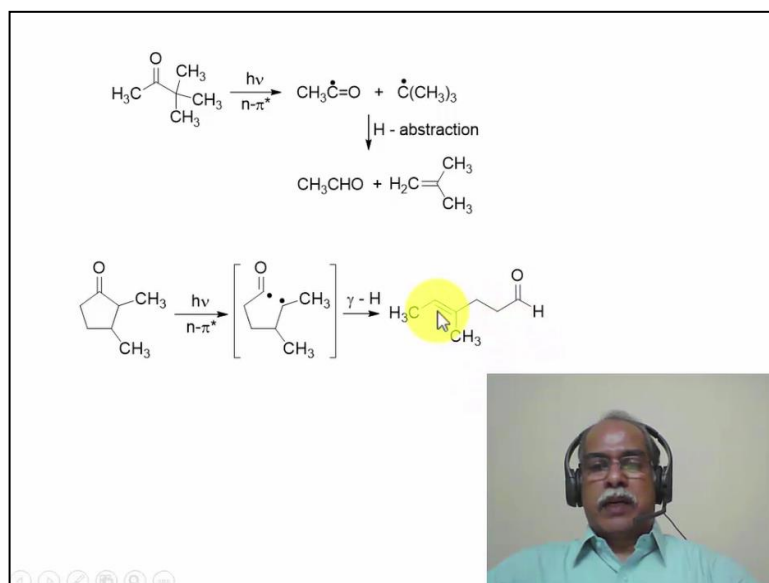
Now, let us go to the, actual reactions. When you take a Tertiary Butyl Methyl Ketone, and do a photo excitation, through an N-PI-Star excited state, which is also the lowest energy excited state, the primary photochemical process is the, excitation to the N-PI-Star excited state, which will have a Diradical character, of this Carbonyl functional group. From the excited state, it undergoes Alpha fragmentation, producing a Tertiary Butyl radical, and an Acyl radical.

The Acyl radical, then absorbs a Hydrogen, one of the Hydrogen, from the Tertiary Butyl group, producing Isobutylene, and Acetaldehyde. So, this is a secondary thermal reaction, is what is taking place. The primary photochemical excitation, is an N-PI-Star excitation. The photochemical process, is the decay of the N-PI-Star excited state, by Alpha fragmentation, to produce this radical. The Hydrogen abstraction, is a follow-up thermal reaction, is what is taking place, to produce Isobutylene, and Acetaldehyde, as the overall products, in this particular reaction.

If you take 2,3-Dimethyl Cyclopentanone, it undergoes Alpha fragmentation, under N-PI-Star excited state condition, to produce this Diradical. There is a Hydrogen, which is available here, which is Alpha Beta Gamma Hydrogen, this particular Hydrogen. So, through a 6-Membered cyclic transition state, this Hydrogen can be abstracted, by the Carbonyl Oxygen, of the N-PI-Star fragmented Biradical.

And, such a Gamma Hydrogen abstraction, essentially produces a double bond, between the two Carbons bearing the Methyl group, and the corresponding Aldehyde is produced. In other words, it produces a Gamma Delta unsaturated Aldehyde, by this process of a Gamma

Hydrogen abstraction, from the Gamma position of the fragment Biradical, that is produced as a primary event.

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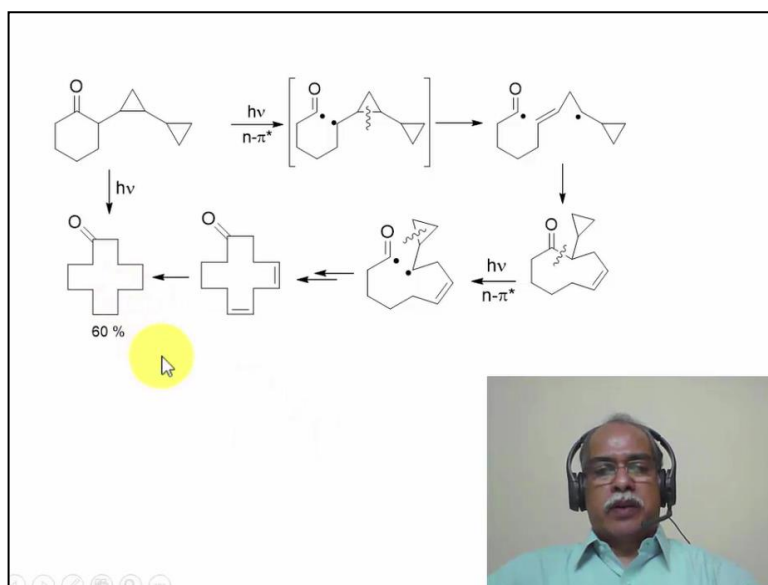
Here is an interesting synthesis of a 12-Membered ring, which is a medium-sized ring, for example, starting from a Cyclohexanone derivative. Photolysis of this particular Ketone, produces this Ketone. There are two double bonds, missing here. I will show the structure, in a minute. How does this proceed? Essentially, N-PI-Star excitation, weakens Alpha bond. Alpha bond fragmentation, produces Acyl radical, and Cyclopropyl Methyl radical.

Cyclopropyl Methyl radical, has the propensity to undergo isomerization, to Butynyl radical, which is this particular radical. In other words, the ring opens, to produce a double bond, between these two. This a Hemolytic ring opening, produces a double bond, and a radical center here, which is a Butynyl radical. Now, this is a 9-Membered Diradical, 1,9-Diradical. The 1,9-Diradical, undergoes a recombination, to produce the 9-Membered ring, again with a Cyclopropyl Alpha substituent, in the Alpha position.

Photolysis of this Ketone, essentially under the same conditions, will result in the formation of another Diradical, which is a 1,9-Diradical. The 1,9-Diradical, will undergo, this is also a Cyclopropyl Methyl radical. So, it undergoes fragmentation process, to give the Butynyl radical. The Butynyl radical, will be a 1,12-Diradical. The 1,12-Diradical, recombines to this. This is an Olefin, that i am talking about, the double bonds are missing.

After Hydrogenation, you get this particular bond, which is a medium-sized ring compound, which is used in the synthesis of Muscone type of compounds. Because, it is a 12-Membered ring, in this particular instance.

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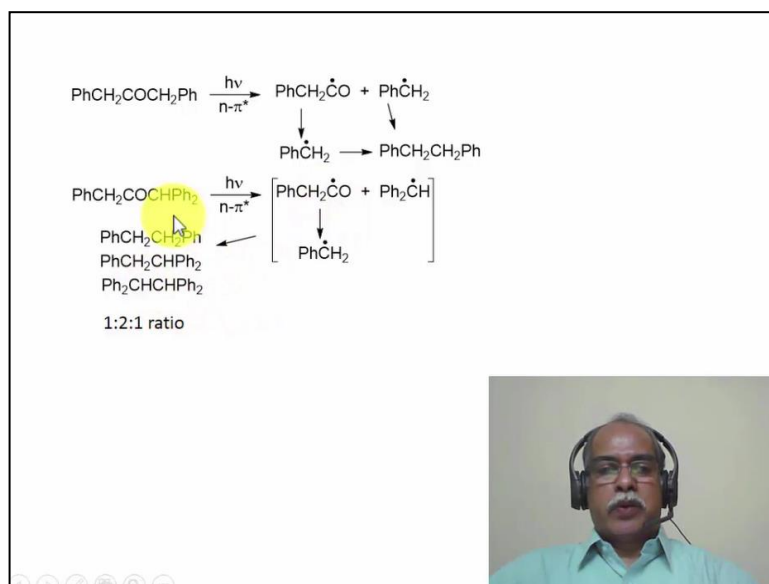
You take a simple acyclic Ketone, like the Dibenzyl Ketone, the N-PI-Star excitation, produces a Phenacyl radical, and the Benzyl radical, by an Alpha fragmentation. The Phenacyl radical, can readily undergo decarbonylation, by loss of Carbon monoxide, to produce the Benzyl radical. The Benzyl radicals, can recombine to give, Dibenzyl as the product. In fact, Dibenzyl is the only product, that is formed, during the course of this reaction.

On the other hand, if you take an unsymmetrical Ketone of this type, the primary N-PI-Star state, undergoes the fragmentation of Alpha bond, this particular bond. Because, this is a Diphenyl Methyl radical that is produced, which is a stable radical. The Phenacyl radical, that is produced, also undergoes decarbonylation, to give the Benzyl radical. Now, the Diphenyl Methyl radical, and the Benzyl radical, has to combine.

They combine, in a statistical ratio of 1:2:1. The major product, that is produced is the, product arising out of the recombination of these two radicals, to produce this compound, which is the Triphenyl Ethane, for example.

On the other hand, Dibenzyl, and Bis Tetraphenyl Ethane, these are the two other products, that are formed, by the recombination of this, and the recombination of this, in a ratio 1:2:1, which is a statistical ratio, that one would expect, from the recombination of Diradicals of this kind, that is produced in the photochemical reaction. So, this serves as an example of an acyclic Ketone, undergoing a fragmentation process, followed by a decarbonylation process, to produce the Hydrocarbons, as the final product.

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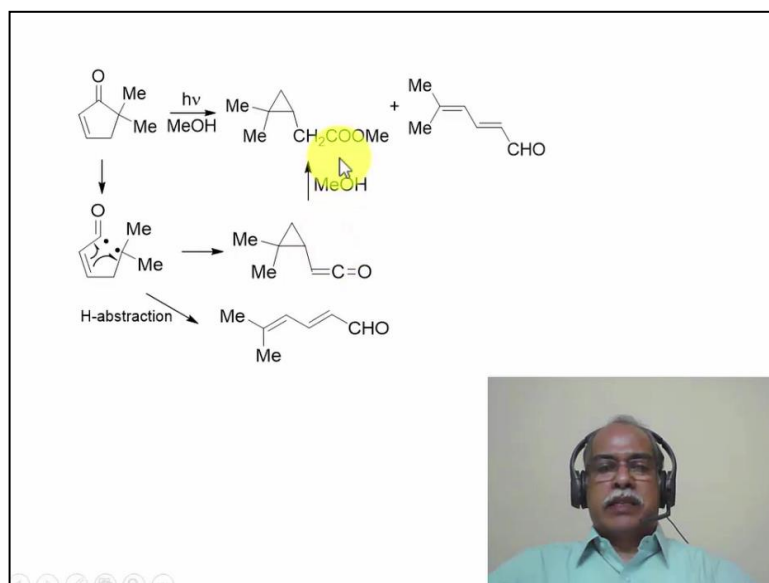
Here is an interesting example of, Alpha-Alpha Dimethyl Cyclopentenone. Cyclopentenone, undergoes Alpha fragmentation, to produce the Diradical intermediate. And, the Diradical intermediate, somehow undergoes two types of reaction to produce, these two different compounds, that are shown here. One is a Cyclopropyl Methyl derivative. The other one is a, conjugated Aldehyde, Diene Aldehyde, is what is produced.

The Diene Aldehyde is produced, by the initial formation of the 1,5-Diradical, which is this Diradical. There is a Gamma position. Alpha, Beta, Gamma, this position has a Hydrogen. The Gamma Hydrogen abstraction, essentially produces the Aldehyde, with a simultaneous formation of a double bond, between this Carbon-Carbon bond, once this Hydrogen is lost, for example. On the other hand, the Cyclopropane derivative is produced by.

This is essentially, an Allyl kind of a radical, if you look at it carefully. So, one can write another structure for the Allyl radical, to produce the Ketene. And, this radical, that is centered here, will undergo the Cyclopropanation, by 1,3-Diradical ring closure, for example, to produce the Cyclopropyl radical. So, imagine that, this is homiletically cleaved, to produce a double bond, which is part of the Ketene, and the radical center here.

And, the radical center now, combines with this radical center, to produce a Cyclopropane, which is this Cyclopropane, that is formed. This Ketene, will not survive under the reaction condition, because it is adding to the Methanol, to produce the Ester. So, the fact, the Ester is produced, is an indication that, Ketene could be an intermediate stage, in this particular reaction.

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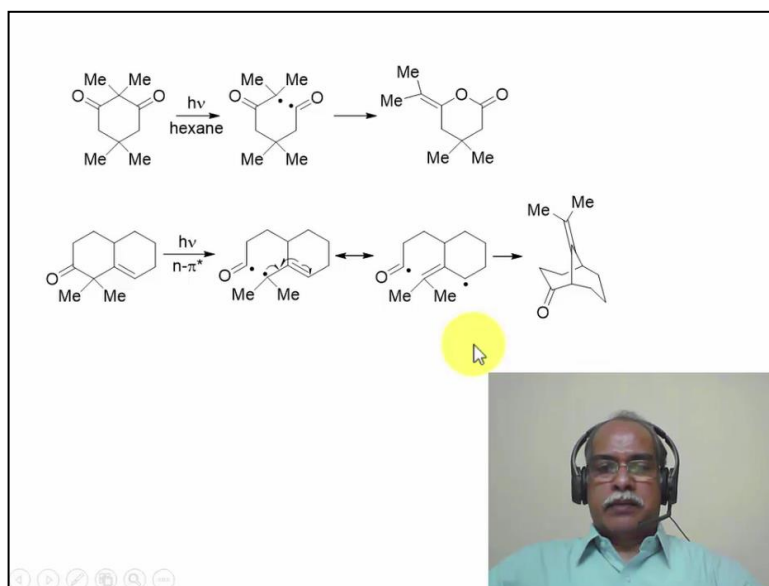
Another example, of an Alpha fragmentation process. This is an, Alpha-Alpha-Disubstituted Ketone, Diketone. It undergoes Alpha fragmentation, to produce an Acyl radical, and a Tertiary Butyl kind of a radical. The Acyl radical can isomerize, i mean, you can write an, Oxy radical here. And, the Oxy radical can combine at this position, to give the Lactone, that is shown here, for example.

So, one can write another resonance structure for this radical, with the Oxy radical produced here. The Oxy radical from this Carbon, essentially undergoes insertion to this Acyl radical, for example, with a simultaneous formation of a Carbon-Carbon double bond, which is appearing as the exocyclic double bond, in this particular case.

The mechanism is shown here, for another reaction. In this particular case, this Ketone essentially undergoes, this is an Allylic Ketone. This is a not a conjugated Ketone. Nevertheless, it is Alpha-Alpha-Disubstituted Ketone. N-PI-Star excitation, produces this Diradical. This Diradical is an Allyl Diradical. This is an Allyl radical. So, one can write a canonical structure of the Allyl radical, producing this reactive Carbon radical, with a exomethylene double bond, here.

Now, this 6-Membered ring can be formed. This is a 1,6-Diradical. So, the 1,6-Diradical, if it combines here, this would appear as a bridging Methylene. You can see here, this would be a bridging Methylene, with a combination of this Diradical, to give this particular product, that is shown here. So, photolysis of this Ketone, essentially produces this as the sole product, through the mechanism, that is shown in the process here.

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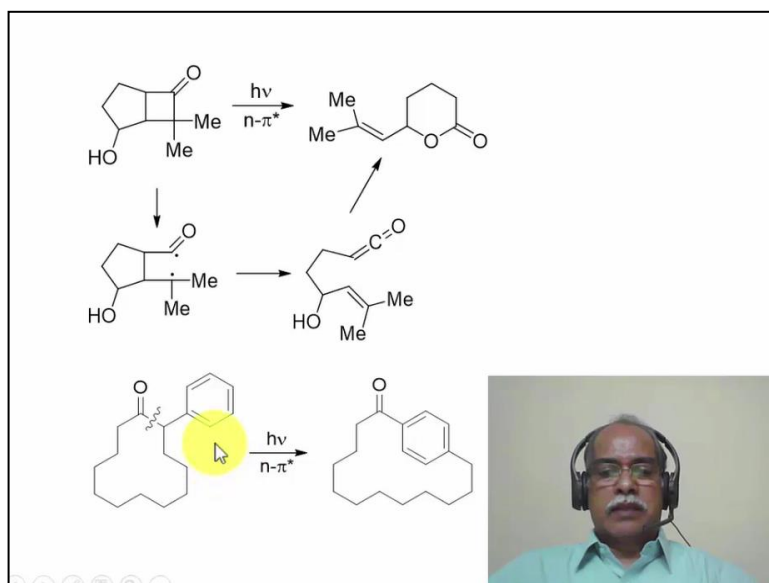
This is essentially, the same kind of a reaction. Alpha fragmentation, produces a 1,4-Diradical. Being, part of a Cyclopentane 1,4-Diradical of this kind, it further undergoes fragmentation of this particular bond, producing a Ketene here, and a double bond here. The Ketene, of course has an internal nucleophile, which is this alcohol. With respect to the Alcohol Oxygen, the Ketene Carbon is 1-2-3-4-5-6. So, it will produce a Delta Lactone, by the recombination of this alcohol, trapping this particular Ketene structure.

So, the Ketene is trapped by the internal nucleophile, to produce the Lactone, which is a Delta Lactone, in this particular case. This is Alpha, Beta, Gamma, Delta, Delta Lactone is what is produced. And, this part of the molecule, essentially appears as a Dimethyl Substituted Olefin, in this particular instance. Another interesting example. This is, Alpha fragmentation of a large Ketone. So much, so that, the length of this Acyl radical that is produced, is sufficiently long to reach the Para position of the Phenyl ring.

So, it attacks the Para position of the Phenyl ring, producing a wheeled kind of an intermediate Cyclohexadienyl radical, which loses a Hydrogen Atom, to produce essentially this particular Ketone. So, this Ketone synthesis, is essentially aided by an Alpha fragmentation, followed by recombination in the Para position, to give a Paracyclophane of this kind. Interesting example. Application of an Alpha fragmentation, towards synthesis, you can say.
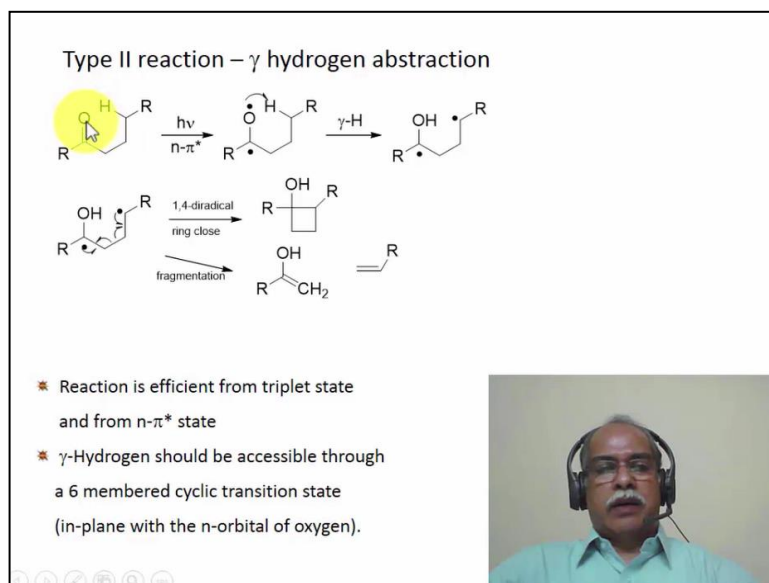
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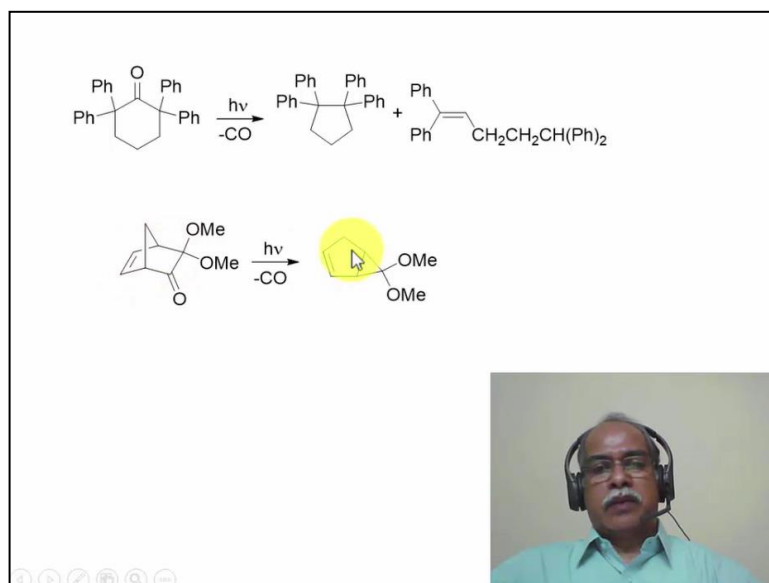
Now, heavily substituted Cyclohexanone, of this kind. This is the, 2,2,5,5-Tetra Phenyl substituted Cyclohexanone. This undergoes Alpha fragmentation, followed by decarbonylation, to produce a 1,5-Diradical. The 1,5-Diradical closes, to give Tetraphenyl Cyclopentane, as the product. Alternatively, it can abstract a Hydrogen from the Gamma position, resulting in the formation of an Olefin, and the decarbonylation.

For example, the Diradical, that is responsible for the formation of this, can abstract a Hydrogen from here, producing the saturated Carbon here, and producing an unsaturated C-double bond-C over here, in this particular instance. Here is an example, where a bridge head radical, that is produced by an Alpha fragmentation process, is undergoing a Cyclopropanation, for example, produce a Diradical here, swing it over here, and form a Cyclopropyl derivative. So, cyclopropylated Cyclopentene, is what is the product, that you get out of this fragmentation process.

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Type II reaction – γ hydrogen abstraction

* Reaction is efficient from triplet state and from n-π* state
* γ-Hydrogen should be accessible through a 6 membered cyclic transition state (in-plane with the n-orbital of oxygen).

Now, let us move on to, type two reaction, which is a Gamma Hydrogen abstraction kind of a reaction. Wherever, there is an accessible Gamma Hydrogen, which is shown here. This is Alpha, Beta, and Gamma Hydrogen. The N-PI-Star excited state, is represented by a Diradical state. This is highly reactive towards, Hydrogen abstraction reaction. That is why, through a 6-Membered cyclic transition state, it is able to access this particular Hydrogen, producing the 1,4-Diradical.

The 1,4-Diradical, has several pathways to decompose. It can undergo, recombination of the 1,4-Diradical, to produce a Cyclobutane, which is happening in certain cases. It can also undergo further fragmentation process, to produce an Enol, which will go to the Ketone, and the Olefin. This is similar to the, McLafferty kind of a rearrangement, is what we have, in this particular instance. The reaction is highly efficient, from the Triplet state, which is also from the N-PI-Star excited state, of the Carbonyl functional group.

Gamma Hydrogen should be accessible, through a 6-Membered cyclic transition state, occasionally from a 7-Membered cyclic transition state also, it is known. The Hydrogen has to approach from the orbital, corresponding to the N-Orbital plane of the Oxygen. In other words, the geometric requirement is, there is a N-Orbital on the Oxygen, and a CH bond should be in the same plane, as the N-Orbital of the Oxygen, so that, it is easily accessed by the Oxygen Atom. That is a stereochemical requirement, of this.

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γ-hydrogen abstraction exclusively from equatorial alkyl group
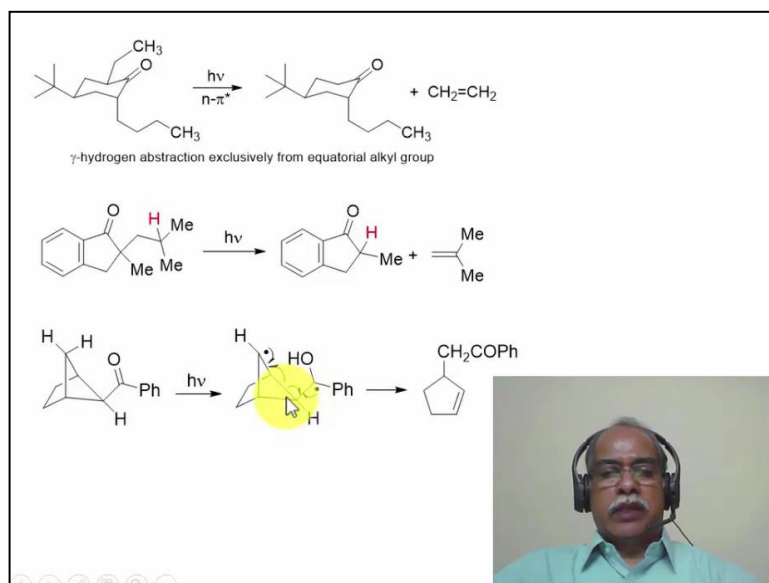
Now, if you have an axial substituent, and an equatorial substituent, the equatorial Gamma Hydrogen, is more easily accessible. So, that specifically undergoes, Gamma Hydrogen abstraction, followed by fragmentation, to produce Ethylene. So, these two Carbons, are produced as Ethylene. The axial substituent, remains intact, in this particular case.

So, this is an example of a conformational accessibility, of the Hydrogen based on, whether it is in equatorial position, or in the axial position of the Gamma Hydrogens, were in equatorial position or the axial Hydrogen. This is a more easily accessible Hydrogen, compared to this particular Hydrogen, in this case. Now, the Hydrogen, that is shown in the red color is abstracted, in this excited state of this particular molecule. And, that transfer of this Hydrogen onto this, will produce a corresponding Enol.

And, that Enol goes to the Ketone, that is shown here. And, the side chain is essentially appearing as Isobutylene, in this particular case. Now, this is a 2,1,1-Bicyclic System. Carbonyl excited state, the N-PI-Star excited state, is represented as the Diradical state, which abstracts this Hydrogen. Because, this Alpha, Beta, Gamma, this is a Gamma Hydrogen. So, the Gamma Hydrogen abstraction, produces the bridging Methylene radical, here.

The bridging Methylene radical, undergoes decomposition, in this particular path way, by breaking this bond, which cleaves the bicyclic system, produces a Cyclopentene with the side chain CH2CO-Phenyl. So, this part of it appears as a CH2CO-Phenyl, by the Enol formation, which undergoes the Keto Enol Tautomerism, to give this particular Ketone.

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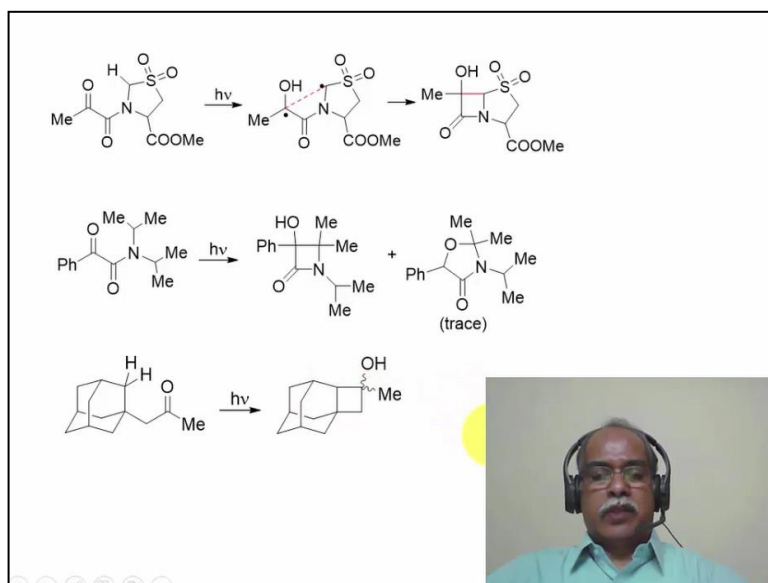
Here is an example of a, Beta-Lactam synthesis, through Gamma Hydrogen abstraction. If you look at this particular Pyruvic Amide, that is formed here, in this particular instance. This is a Gamma Hydrogen. Photo excitation, of this Carbonyl functional group. There are several, Carbonyl functional group. But, this is the only Carbonyl functional group, which has an accessible Gamma Hydrogen. So, the 1,4-Diradical, that is produced, undergoes ring closure. The red bond, is the newly formed bond, as a result of ring closure, resulting in the formation of the Beta-Lactam, in this particular case. Similarly, if you take the corresponding Phenyl derivative, the Beta-Lactam is a major product. However, a minor amount of this Oxazolone is also formed, during the course of the reaction. This product is formed, essentially by the Hydrogen abstracted, from this position on to the Carbon, followed by a ring closure, across the Oxygen-Carbon bond, which is this particular bond, here.

This is an adamantine case. Adamantine with a side chain, which bears a Ketone. This is Alpha, Beta, Gamma. This is a Gamma Hydrogen. The Gamma Hydrogen abstraction, followed by a ring closure, essentially produces this particular Ketone. So, it will produce a 1,4-Diradical. That 1,4-Diradical, undergoes recombination, to give the Cyclobutane ring, with a Hydroxy and Methyl substituent on the Cyclobutane ring, which is shown here.

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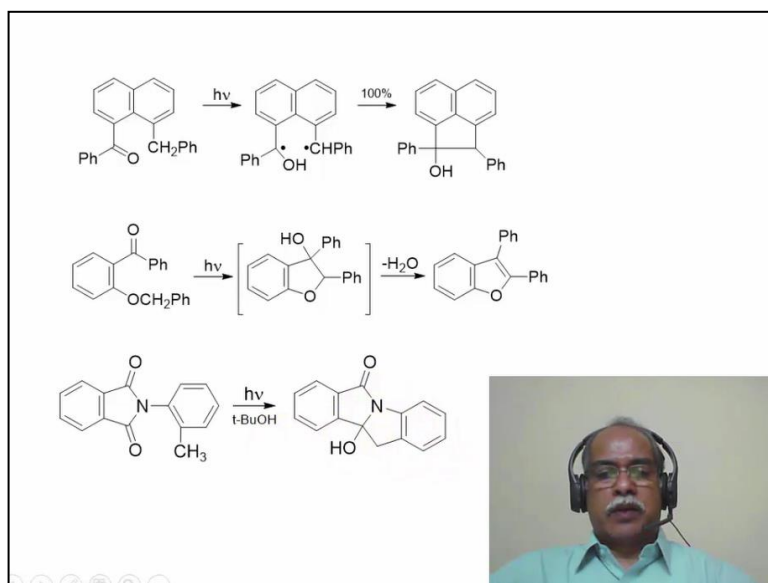
Many more examples of, Gamma Hydrogen abstraction. This is not a Gamma Hydrogen. If you look at it, this is Alpha, Beta, Gamma, Delta. So, this has to come through a 7-Membered ring, in this particular case. Nevertheless, because it is an intramolecular process, it is extremely efficient. The Diradical, that is produced, is a 1,5-Diradical, which undergoes recombination, to give the Sigma bond, which produces this particular Pentane ring, with the substituents coming from the Ketonic positions here.

Another example. This is the, Benzyl Oxy substituted, Benzophenone. Upon photolysis, N-PI-Star excitation produces the corresponding Carbonyl excited state, which abstracts the Hydrogen from the Benzylic position, which is this position. So, it undergoes 1-2-3-4-5, 1,5-Diradical, undergoes recombination, to form this Benzofuran ring. During the chromatographic separation, this essentially undergoes dehydration, in the presence of silica gel, to produce this particular compound, which is a Diphenyl substituted Benzofuran derivative.

Here is an example of Phthalimide. This is Alpha. This is a N-Tolyl Phthalimide, is what is produced here. This is undergoing the photochemical reaction, in Tertiary Butyl alcohol. The N-PI-Star excited state, produces the Carbonyl excited state, which abstracts Hydrogen from the CH2, followed by a 1,5-Ring closure, to produce this 5-Membered ring, in this particular case. Synthetically, these are extremely useful reaction, to produce this kind of fused ring systems, of this kind.

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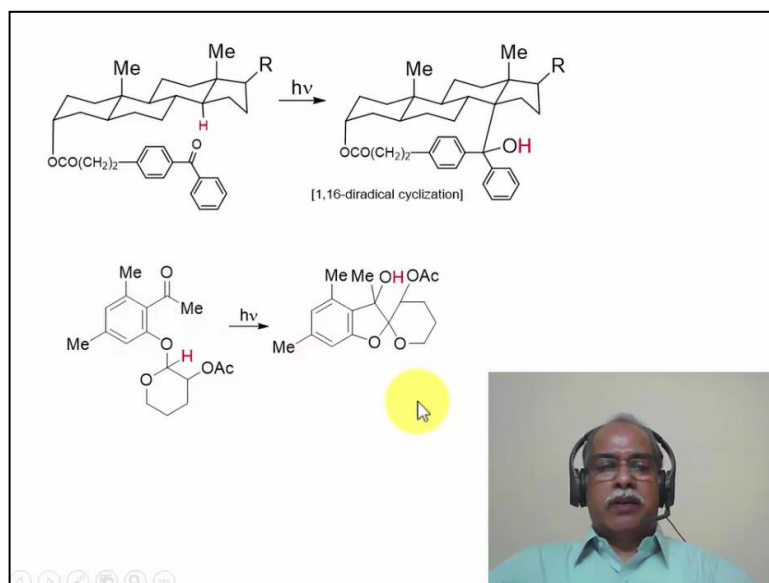
Here is a beautiful example, a tailor-made example, which produces a 1,16-Radical. In other words, this is a Hydrogen, which is accessible, because of this long chain, of this Benzophenone derivative. This is a substituted Benzophenone, where the skeletal structure being a rigid structure, puts this Hydrogen, in close proximity to the Carbonyl excited state. In the excited state, the Carbonyl Oxygen can access, this particular Hydrogen.

The geometry is such that, the length of this molecule is such that, this Hydrogen and the Carbonyl Oxygen, come close proximity. In the excited state, it produces a 1,16-Diradical. It undergoes cyclisation, to produce a macrocycle, which is a 16-Membered ring, is what is being produced, in this particular instance. Another example of a, Delta Hydrogen. This is, Alpha, Beta, Gamma, Delta Hydrogen abstraction, producing a Spirocyclic ring system. It is a very synthetically interesting ring system, that is produced, during the course of this.

So, the Gamma Hydrogen abstraction, produces the corresponding alcohol, which produces the 1-2-3-4, 1,5-Diradical. The recombination of the 1,4-Diradical, essentially produces this Benzofuran ring, fused with the Pyran ring, as a Spirocyclic system, in this particular case. Very interesting example, of a Hydrogen abstraction reaction, of an excited state Carbonyl functional group.

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Demonstration of reversible type 2 hydrogen abstraction
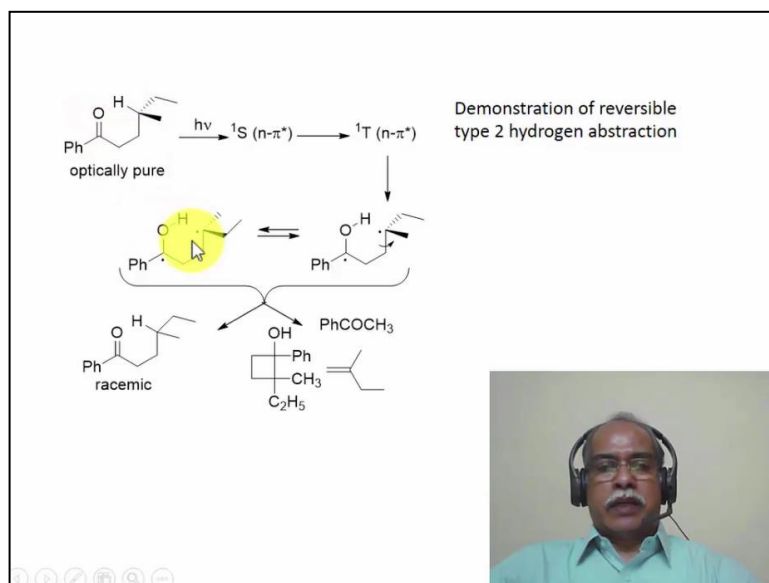
Now, whether the Hydrogen abstraction is a reversible process or not, is easily demonstrated, by taking enantiomerically pure Ketone. This is a chiral Ketone, because of the chiral center here. Now, what needs to be done, is to do the photolysis, and recover the unreacted starting material, and see whether it is optically pure or not. The reason is, like this. When you do a N-PI-Star excitation, it produces a Singlet state. By Intersystem crossing, it produces a Triplet state.

The Triplet states, undergoes the Hydrogen abstraction, that is shown here, and produces a 1,4-Diradical. At the 1,4-Diradical state, there is a free rotation of this Carbon-Carbon bond, which will racemize this particular molecule. Because, this becomes a planar Carbon, and undergoes racemization, quite readily. Such a racemization process, if the Hydrogen transfer is reversible, it will produce a racemic Ketone.

And, when it undergoes a fragmentation process, and recombination process, these are the normal products of Norrish type two reaction. Whereas, this is an unreacted starting material, which is a racemic starting material. In fact, when the photolysis was carried out, and taken not to completion, when the unreacted starting material is recovered, that was found to be racemic, indicating that this Hydrogen transfer abstraction, and a back transfer to the Carbon center radical, is a reversible process.

So, because at the 1,4-Diradical state, it can undergo racemization. The reverse reaction, essentially produces a racemic Ketone, indicating, that the Hydrogen transfer is a reversible step, in this particular case. This is a racemization step, that is shown here, as a reversible stage. The Hydrogen transfer, you can also draw a reversible arrow, between the excited state, and this molecule, in terms of the Hydrogen, being picked by the Oxygen, in this

particular case. The reverse reaction, the Oxygen donates back the Hydrogen, to this particular center.

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Stereochemical consequence of Type I vs Type II reaction of carbonyl excitation
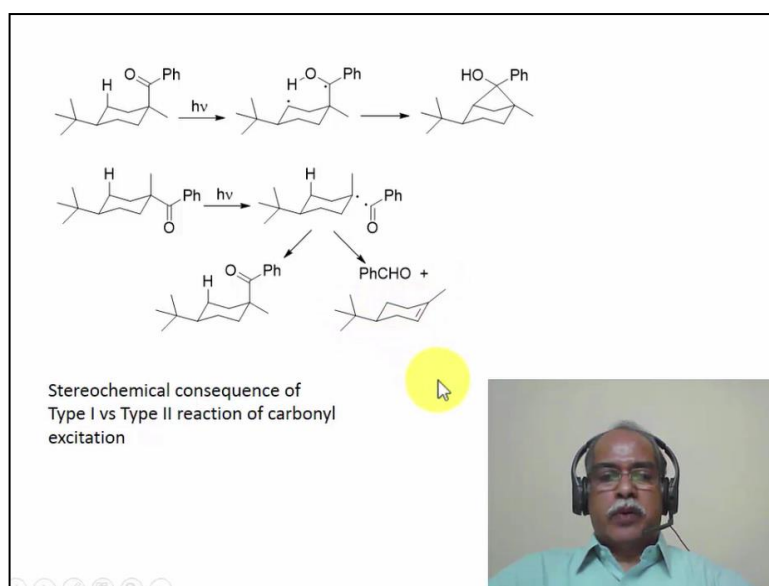
Now, stereochemistry has a direct consequence on the type one, and type two Carbonyl excited state. Take this two examples. These are Diastereo isomers. This is an axial Ketone, whereas this is an equatorial Ketone. Photolysis of the axial Ketone, produces only this molecule, here. How is it producing? It has an accessible Gamma Hydrogen, which is an axial Hydrogen. Both are axial substituent. So, you heard about the 1,3-Diaxial interaction. This is a Tertiary Butyl anchored Rigid system.

It cannot undergo, chair to chair inter conversion, like Cyclohexane does. So, this will stay in this rigid confirmation. And, because the close proximity of this Hydrogen and the Oxygen, in the excited state, it will undergo the Hydrogen abstraction reaction. And, the 1,4-Diradical will essentially close, to give this fused bicyclic system, that is shown here. This is a 4,1,1-Fused Bicyclic system, is what is given here. Bridged Bicyclic system, is what is given here.

This is an equatorial Ketone. The equatorial Ketone, does not have an accessible Hydrogen, because this is equatorial. The equatorial Hydrogen, is not easily accessible. This Hydrogen, or this Hydrogen, is not easily accessible, to this Carbonyl, unlike the axial Hydrogen, and the axial Ketone. So, it primarily undergoes the fragmentation process. Recombination will produce, other Diastereo isomer.

Because, now you can recombine from the equatorial position, to give back the starting material. Or, it can recombine from the axial position, to give the axial Ketone also. And, it also undergoes, the Hydrogen transfer from this position, to produce the Olefin, which is a 4-

Tertiary-Butyl-1-Methylcyclohexene, is the product. Benzaldehyde is the other product, arising for the Hydrogen transfer, between these two radical centers, in this particular case.

So, the axial Ketone produces, only this Bridged Bicyclic Ketone. Whereas, the equatorial Ketone, essentially produces not only the axial Ketone, but the other products, Tertiary Butyl, Methyl Cyclohexene is also produced, in this particular case. What if, these two Ketone are equilibrating?

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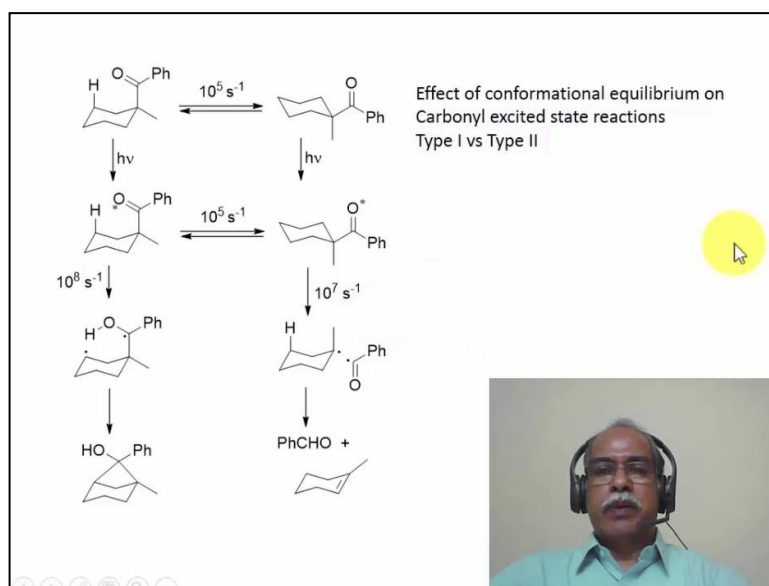
That is shown, in the next slide. In this particular instance, this chair to chair inter conversion, is very facile. And, of course, this is a not the preferred confirmation. This would be the preferred confirmation, with the bulky substituent, in the equatorial position. Nevertheless, this equilibrium takes at the rate of about 10^5 per second, in terms of the rate of this reaction, equilibration for example.

Now, when you fertilize this mixture, both the Ketones will undergo photo excitation, to produce the corresponding excited state, which is the N-PI-Star excited state. However, because the axial Ketone has an accessible Hydrogen, the rate of Hydrogen transfer is very fast, in this particular case, 10^8 per second. On the other hand, the Alpha fragmentation process is a relatively slower, for example, producing this Diradical center.

So, the product distribution in this particular case, is a reflection of the population of these two states, rather than the population of the ground state. For the simple reason, the ground state can equilibrate, very readily. The excited state, can also equilibrate readily. However, this conformer reacts much faster, so the equilibrium will shift towards this. So, the quantity of the product that is formed, from the axial isomer, is a major product, in this case.

The one, that is produced from the equatorial isomer, is the minor product, because of the fact, the population is not the one, that is governing. The rate of the reaction, is what governs the quantity of the final product, that is produced. Since, the rate of this is about an order of magnitude faster, this will be the major product, that is formed, in the reaction. Although, the population of the axial Ketone, is not as major as the, equatorial Ketone.

The product is formed, from the axial Ketone, because of the fact, this rate of the Hydrogen abstranded reaction, is the order of the magnitude faster than the, fragmentation process of the, equatorial Ketone. So, here is an example of the, conformational equilibrium effect, on the Carbonyl excited state reaction, of type one versus type two. So, what we have seen, in this module, is essentially two important reactions of Carbonyl functional groups, namely Norrish Type One, which is an Alpha fragmentation process.

Norrish type two, which is a Gamma Hydrogen abstraction, followed by subsequent reactions of the 1,4-Diradical, that is produced. We have seen the effect of, the electronic state. We have seen the effect of, bulky substituents, in the Alpha position. We have seen the effect of, the conformational aspects of the Ketones also, in this particular module. I hope, you enjoyed this module. Thank you very much, for your kind attention.