Organic Photochemistry and Pericyclic Reactions

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Module No. # 01

Lecture No. # 07

Cleavage

In this class, we will start with discuss about Beta Cleavage Reaction. So far, we were dealing about the alpha cleavage, so will start dealing with beta cleavage reactions. As they have in the case of carbonyl compounds like, if you have carbonyl compounds in which your C alpha and C beta bonds are weak, that type of carbonyl system can undergo a beta cleavage reactions.

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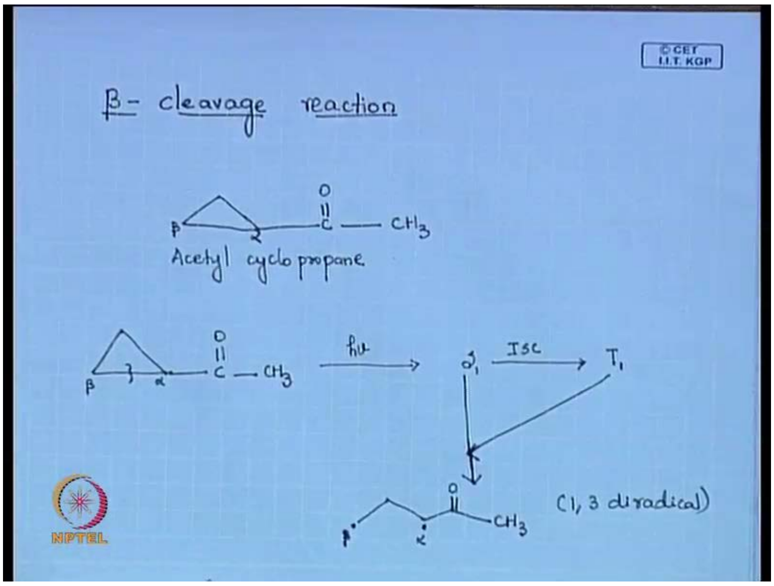

I will just draw a structure so that you will, so this is acetyl cyclopropane right. If you have system like this and if you if you see the system, you can see this is your alpha and this can be your beta, this is C alpha and C beta bond or you can write this alpha and beta. Since the system is symmetrical, there is no need to worry about that part, so if and you know that because of your ring strain, this alpha beta bond is weak (No Audio From

01:07 to 01:18). If you have this type of systems, then you can see beta cleavage reactions taking place. So, a carbonyl system where you have C alpha and C beta bond weaker in that time when you excite the carbonyl, you will get chemistry from beta cleavage reactions. Now, we will take the same example and see how the chemistry work, I have taken my acetyl cyclopropane have a shining like h mu, so what happens, as you know that this carbonyl gets excited to its singlet S 1 and there are cases where it can undergo intersystem crossing to triplet.

See, in case of this type of system, you can see chemistry happening both from your singlet as well as triplet, it is not free dominantly it happens from triplet, you can get some cases from singlet also. How this chemistry happens, basically once your carbonyl is gets excited, now the carbonyl is in the singlet state as well as in triplet state, it has an excited energy this excited energy is then transferred to your C alpha and C beta bond, and that is how the alpha beta bond gets clean.

So, it is a type of an energy transfer, taking from your excited ketone to your C alpha and C beta bond which makes the chemistry to occur. So, once I have now triplet state, I can say that it can happen from S 1 as well as T 1 depends upon your ketone to give me what, I can cleave this bond this is my beta and alpha bond, what I should get, I should get if I break this, so I get this (No Audio From: 4:24 to 4.35). So, what is this? This is your 1, 3 diradical fine, so this is your photochemical process; actually seeing this, this is your primary photochemical of process, then what happens then you see your what this radical chemistry happens. See, till now the photochemistry happens, after that as we said what is going to happen to my radical then?

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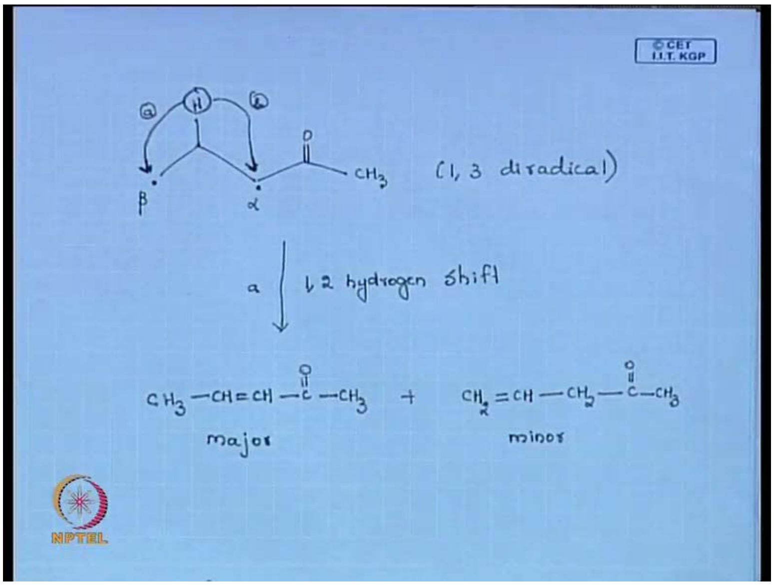

So, what we can, what this 1, 3 diradical does, because you studied about 1, 3 diradical what it can do? 1, 3 diradical, we have studied 1, 5 diradical, we have studied 1, 4, we have studied 1, 3 diradical, so what this 1, 3 diradical does? It cannot do a recombination or cyclostation again to give back your cyclopropane, because that is a ring strain one or what it can do, which you have studied like, now you can do your 1, 2 hydrogen shift that is you normally see, this hydrogen can be shifted, it is a radical, so you can do a 1, 2 hydrogen shifts.

See, the idea is that, you should know what this radical simple adjust, what 1, 5 diradical does, what 1, 4, what 1, 3 you should know this 3 radicals, then you are most of time you are, once you know the photochemical then you are, any how you are going to generate your radical, then just by radical knowledge you can do this chemistry.

If I shift this hydrogen, there is a 1, 2 I call this as a, then I will get a product like C H 3, C H double 1, C H I will get product like this right, so I can call this a, I can also shift my hydrogen like this also know, it is sorry it is a radical I can shift like this also, if I shift in that case, then I will get C H 2 double bond C H.

So, I can think of getting two products now, just by 1, 2 hydrogen shift, so I know the idea of 1, 3 diradical. If it is a 1, 3 diradical, I will be most of time going for hydrogen shifts. So, just I have to see, how this hydrogen shifts, there are two possibility a and b, so I get a type of alkene which is internal, I will get an alkene which is terminal. So, you know internal alkenes are favored right. So, I can say this is your major product and this will be your minor one clear, so this is the simplest example to do this chemistry. Now, we will take some more examples, and will see how this works or we have sure with our alkyl chemistry.

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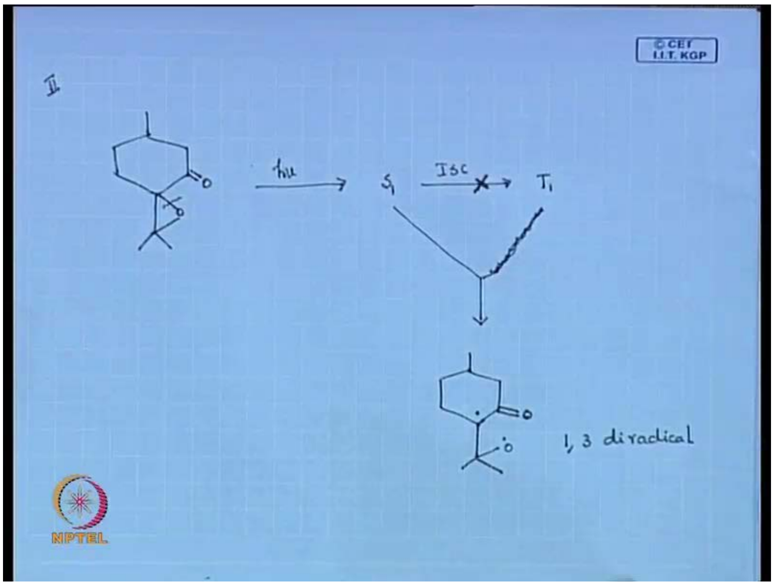

We will take our second example, you can take an example like this, now we will see a this ketone, how it works, so as I said once I photolyse it goes to S 1, then it can get intersystem process to T 1, both the chemistry photochemistry can happen from the both the states, just for it can happen pre dominantly from S 1 and T 1, so you can then get your beta cleavage, so what beta cleavage I am looking for here?

So, which is the weakest bond?

Carbon

Carbon oxygen, so this will be your weakest bond, so I can break this bond right, yes or no,?

See, the average strain you want to break a C C bond or you want to break C O bond?

C O bond

C O bond, so I am just breaking my C O bond.

See, it is a typical epoxy ketone, know so I can get this step of radical now, ketone like this type of system. So, what we call this again, see sorry in this case for just a just a minute, in case of epoxy ketone, you never get your intersystem processing to triplet, just that is this step never ever happens the case of epoxy ketone. If it is a cyclopropane system yes, you can see intersystem process, but in the case of epoxy ketone, your singlet state dominates the chemistry. So, you see always your chemistry happening from S 1 not from your T 1 fine, so you just cross this, so this is not going to a happen in the case of epoxy ketone. So, whatever I am getting, I should get from my S 1 state yes, the chemistry same it is n pi star, S 1 n pi star again it is a 1, 3 diradical (No Audio From: 10.20 to 10.36).

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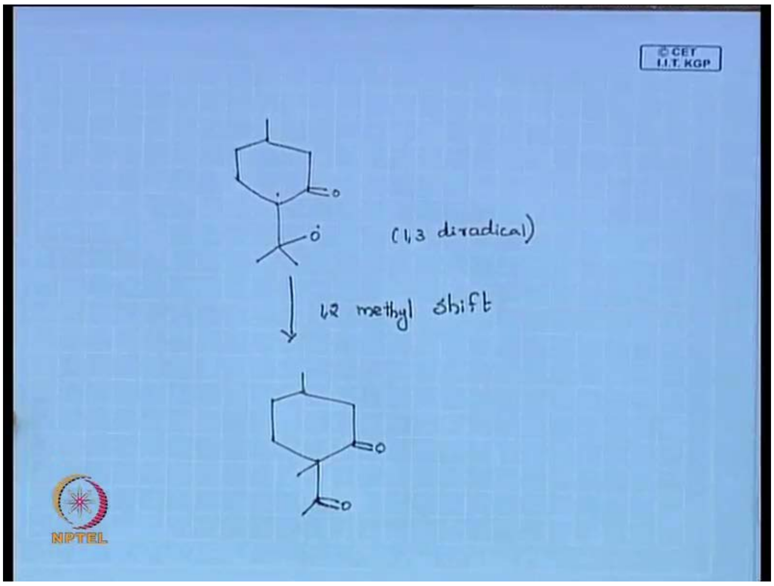

So, what now this 1, 3 diradical can do? What this 1, 3 diradical can do now, is there any hydrogen I can figure out here? See, this is my radical right 1, 2, 3. I do not have hydrogen here. Then it does a 1, 3, 1, 2 methyl shift instead of hydrogen shifts I can do my methyl shift, so you can do 1, 2, if I do 1, 2 methyl shift, so I can shift this methyl, so I get a di ketone type of system, any doubt in this example? See, you have basically I have taken one example where I dealt with cyclopropane system. Now, I am taking in a example, I am dealing with epoxy ketone system and I said in cyclopropane system, the photo chemistry can work from S 1 as well as T 1.

But in epoxy ketone system, it works mostly from your S 1 state, but in the both of the case you are getting 1, 3 diradical, in one case you are shifting your hydrogen, in another case your shifting your methyl that is all. So, these are two main things you can see in beta cleavage, so based on this we will do now n number of examples, we will do some examples based on this knowledge.

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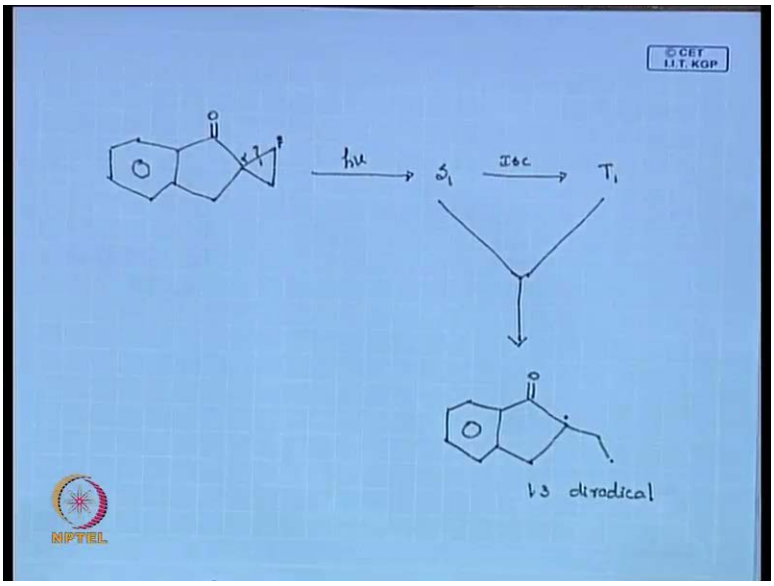

This is the two broad class of a ketone which does beta cleavage reactions, so I have a system like this, so what you say, this is an example of your cyclopropane right; the class of ketone having cyclopropane. So, then what you say of the photochemistry can work, we will say that it goes to S 1, it can undergo an intersystem crossing it give my T 1 and the chemistry can happen from both my excite states. So, it give me a bond cleavage, so I want to break my bond, so this is alpha and this will be beta, can I cleave here? I can cleave this, I get a 1, 3 diradical (No Audio From: 15.15 to 15.38).

Now, think what you can do with this 1, 3 diradical, can you write by yourself, what this 1, 3 diradical can do? sorry I missed my aromatic, just a minute, I have missed my aromatic in the earlier case sorry, so type of aromatic system.

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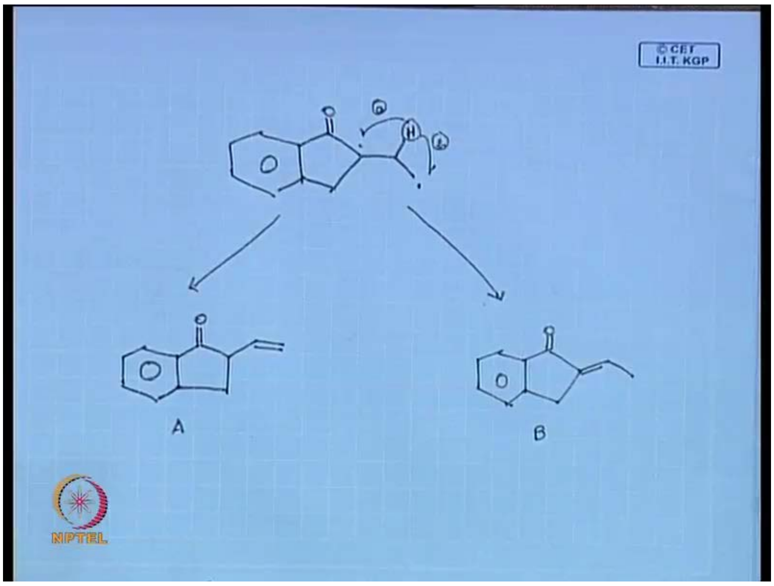

What this molecular can do now?

Write like all the products, like what you can think and say me which will be the major and minor you can think about. So, I can put my hydrogen here, so I can write two products now, I can write a product moving this hydrogen here or I can write a product moving this hydrogen to this 1, 2 hydrogen shifts, I can do in both the base. So, if I move my move I can call this a or I can move I call this is b, for this (()) you can move my hydrogen that this direction and you can get a alkene like this yes; other way round system, we can get the, so we can get two products right, now so which you think like can be more or major yes, I can call this as a, I can cal this as B, B because you know that alkenes internally much more stable fine, that is correct.

Hydrogen can be

(())

C H 2, C H 2 which C H 2 you are talking about this hydrogen

(())

This hydrogen

(())

You want to abstract this hydrogen for what

(())

No, it does not happen from here most of the time, because it is just your alpha beta, your first photochemical process, you are getting only 1, 3 diradical.

Why you want to move 1, 3 diradical here

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Yes, you want to abstract this hydrogen fine

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You want to take this radical and abstract this one, then what you want to do; you want to create an alkene, how?

See, you want have a other radical is there in the system right

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You want to abstract this hydrogen and make a this one, you think it is possible it as to bend down, in this case it never does whatever your thinking is fine, you can take this hydrogen here and then you can generate an alkene that is also possible, but in this case it does not happen. Radical chemistry, when you are writing radical chemistry that is why I said write all your products, nothing wrong in it.

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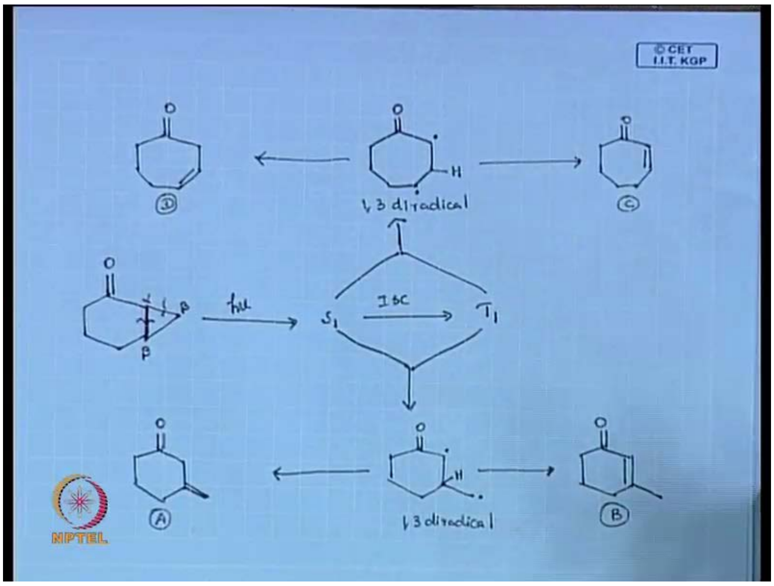

So, I have a system like this now, what it can do, so once I photolysis again I said that you know all this things that it gives S 1 then intersystem then we see T 1 fine then depending upon your molecular, you can get from your S 1 to T 1 (No Audio From: 20.13 to 20.24). So, I can write here, the system of what I can call this alpha, beta right, so can I cleave this, you can get this fine from this I can write two products have a hydrogen here, I can shift it this direction to get and in like this.

See, first will write all this products, then will decide like which will form more or not, an alkene like this or I should get system nice alpha, beta; now you know, that among this will be form, we can call this a, we call this B you can clearly say B will be formed as a major product.

Now, if you think this chemistry little bit carefully, I have another chance of cleaving my bond, you see I have cleave alpha, beta, if I cleave this one, what happens? This is also an alpha beta bond, this one this particular that also be an alpha beta bond as I said this is alpha beta, this is also an alpha beta in previous case, it was so symmetry that if you break on both the side it as same.

But in this case it is different, I if break this one then what happens, if I break from here, what I should get, can you write I can get like this yes or no, see that is why I said; see if you have different example will tell you many ideas like, a it is not only you have to look for one alpha beta bond, there is a another alpha beta bond also (No Audio From: 22.53

to 23.05). So, you have to do that chemistry also, you get system like this now you have an hydrogen, so what it can give you again I think of two products, because again it is a 1, 3 diradical; like this is 1, 3 diradical again I can call this also 1, 3 diradical, so can write two products when I can shift my hydrogen here right, so I can take simple chemistry now, like I have take an side a ketone system with a cyclopropane and I am saying that C you can get now four products A, B, C and D, so this are all possible products; then once you go to lab and we do the reaction then you will know which will form major, see if you see from here I can say B C D can be form without any problem (No Audio From: 24.01 to 24.19) yes. So, that is how you should know, how this see the chemistry, photochemistry here is very simple just it goes by S 1 and then intercession cross with T 1 to give me a 1, 3 diradical.

Then what I am going to do with this 1, 3 diradical, that is how where the chemistry starts; I say 1, 3 diradical now you will know it is does hydrogen shift nicely, so you have to do in both the possible ways, because you will get a two radical 1, 3 diradical and your hydrogen will be the middle, so you have to do in both the ways then the care should be taken that if you have other alpha beta bonds then you should involve that also clear.

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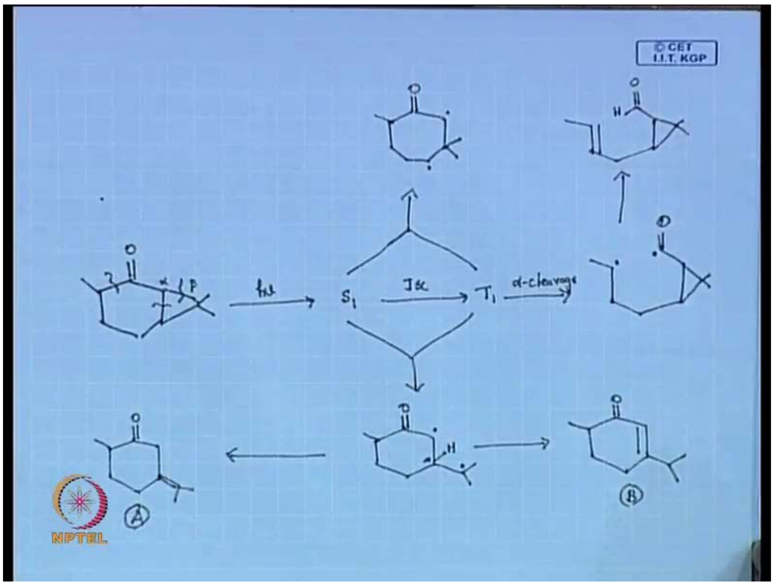

Now, will take one more another examples, I should think about just like prevail case I will take if you compare this example with the previous example, I just like the similar system, but I have like a methyl subsidiary iron there, so you should understand why I have said, what will do, what this methyl as some influence or not. So, once which then you are fine, you do your first step that is S 1 right.

So, I can call this alpha beta and I am braking down this one then a radical, I can take a radical no sorry, I can take radical here, I can get radical here, yes then I have an hydrogen here (No Audio From: 26.45 to 27.08). So, you can write two products then you can see initially you try to write all the products such where, then decide, then understand which will be the good one; so you can get nice work, if I move this hydrogen across here, I can get one product like this yes or I can think of a another product where I have an alkene outside yes, if I move this hydrogen this to my cyclopropane, like a my secondary isopropyl unit then I will get a system like this or if move my hydrogen here then I will get an system with alkene outside (()).

So, from the structure itself you can cleanly say that, which you want to, so it looks B to be formed in major, now you have the another question you have to ask yourself, I have another alpha beta bond here, can I break this whether the molecular tries to break this alpha beta bond, previous case I have broken this bond I have got cyclohexane type of system cyclopentane type of system.

In this case, can I can break this just try, just try and see what you get, why you should not break, if I break this bond what I should get radical here, I can get a radical here with my, so why you do not want to break this?

No hydrogen

No hydrogen is there, so you do not want to break this that is how criteria yes right.

So, I cannot write any other product, so based on this that is why the molecular says I am not going that side, now this molecular can do any other chemistry.

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No, I am talking about photochemistry any other photo reactions can these molecules do

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See that is what because, in this class we are just thinking about beta cleavage, we just our eyes goes only at beta cleavage, why this molecule do alpha cleavage see I just made this molecules so nice that it as methyl there, so that whatever radical is form that radical can get stabilize, so why cannot this molecule do, now alpha cleavage reaction it can do pretty well alpha cleavage.

That is why you put a methyl there, so there are reactions where you have to complete your alpha and beta cleavage; it is not that you see today I am taking a class were I am taking only beta cleavage, so I am taking only beta cleavage example but, your molecule does not do like that, so whatever feverous it does it does alpha cleavage as well as it does beta cleavage.

So, if then so I can do alpha cleavage here, because I know that I cannot do an alpha cleavage in that direction, I can do alpha cleavage here, because I get stable radial system like this; and you know pretty well, what this does I can abstract an hydrogen to give me a aldol right, that is what we study in alpha cleavage reactions, then you can say can decarbonylation all this process can happen.

But, you should know yes this also undergoes a alpha cleavage reaction, so I will leave you with this radical you can do any, because you study what this radical can do, it is it is one you can decarbonylation then you can see what radicals you are getting up, then you are have studied what (()) it does it can abstract an hydrogen acyl radical can abstract an hydrogen, if acyl radical abstracts an hydrogen then what you get, you get an aldol in right.

If alkene radical abstracts, then what you should get, but in this cases we do not get that possible ketone right so that all you have to no work on this, and find out what are the products it can be right. So, major major product you get out of this is get, this is an nice aldol process think of writing a straight chain then you will right, looks like simple molecule and I am trying to do all the chemistry here, I have generated some different radical from here, from here you can generate 1, 5 diradical also (No Audio From: 32.42 to 32.54).

So, when when a molecule is given you put your mind and see whether it undergoes all other chemistry, now your studying only alpha cleavage reaction and beta cleavage reaction, in next class you will be studying hydrogen abstraction reactions then you should know, because all this chemistry is done your carbonyl only. So, your carbonyl can, and then you should understand whether my carbonyl system will do alpha cleavage or beta cleavage or it will do intermolecular hydrogen abstraction, what type of chemistry.

All whether it will do, all this things together

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That also happens, so it becomes nice once you go for good examples

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Beta cleavage, there is a computation, but you can get beta cleavages more products, both are fissile, the products in this case beta cleavage for you get more.

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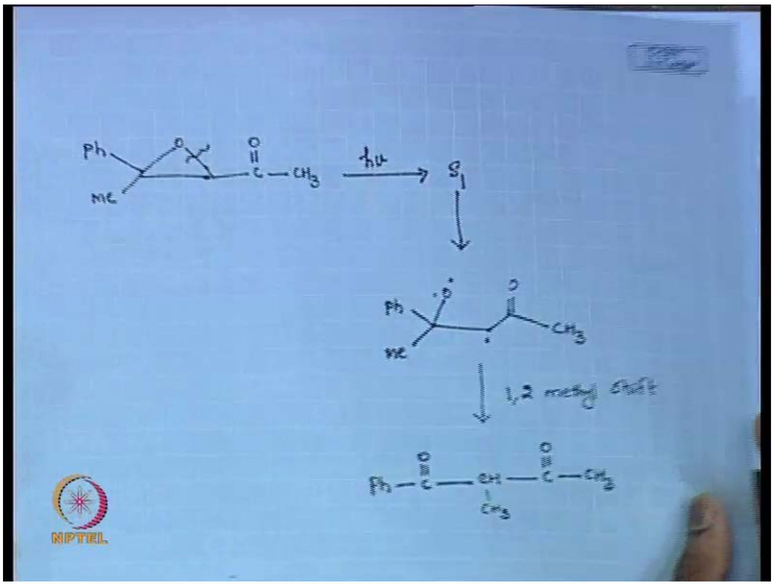

Now, will take simple example, let be a little bit simplest examples, so that this is you remember what we learn in 5 minutes before, so what you do, so shall I once I shine light I will say that I will go for S 1, then I do intersystem crossing to T 1.

No, because it is a

(())

epoxy ketone that is good. So, you remember then and now from S 1, I can do my cleavage, so in this case you know that I can cleave with this C O bond is little bit big, so I can get up radical, what radical I can get I can get a finale methyl O dot look, like same this term.

Now, now it is again 1, 2, 3, 1, 3 diradical system, what you are preferring to do here 1, 3 diradical system.

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So, you want to shift your methyl, why you are not shifting you are your finely

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You have an option here right I can say that I am doing

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1, 3 1, 2 methyl shift you are doing, I am asking why cannot you do 1, 2 finely shift anything wrong

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Yes, will do that is what you have to remember, if instead of my finale if have some other molecule then you have to always you should not think about moving only your methyl, it depends upon which undergoes frustration; in this case it is methyl I cannot take my finale dot it is very happy generator. So, that is my product alkene, so with two basic ketone I am working on, one cyclopropane ketone another alkene one epoxy ketone, we saw 1, 2 hydrogen shift, we are now seeing 1, 2 methyl shifts, normally you can call it as 1, 2 alkene shifts there are many cases where it happens fine.

Now, will see another example where you are not doing your 1, 2 methyl shifts yes

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The previous example, you yes

(())

You want to break

(())

Which this bond, but this is the weakest bond no

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See stability, but you are bond also plays a important role why this energy transfer happens, normally the energy transfer happens then your weakest bond weeks.

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This side is not alpha beta energy, so energy transfer does not happen there this you can see from your UV spectrum, normal ketone have like once in UV spectrum, you can see this epoxy as well as cyclopropane have influence on the carbonyl, you can see your shifts this factor that is how you find out there is energy transfer taking place.

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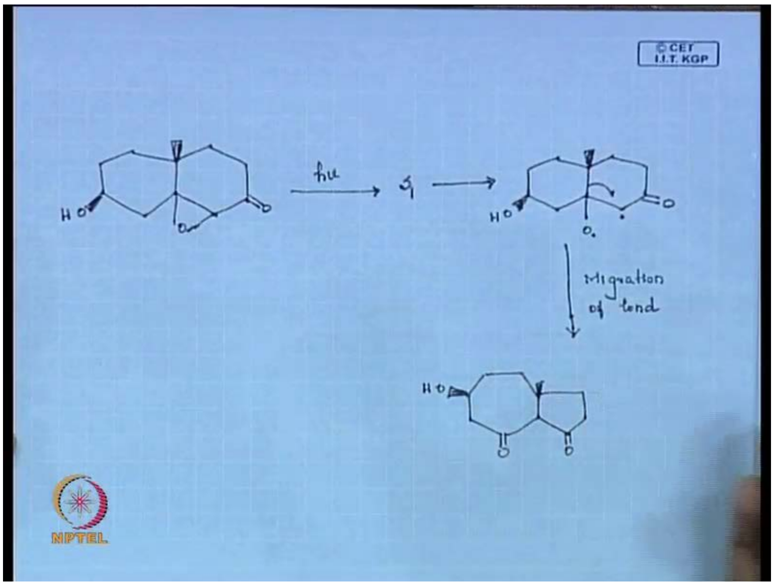

That is good; yes keep on thinking in that way it is nothing wrong in it, so I have system with epoxy ketone like this, so what it can do now, you say it is a photolysis equals to S 1 from my S 1, I can get so I getting system where, again I am getting 1, 2, 3 diradical right, 1, 2, 3 diradical system (No Audio From: 38.52 to 39.12). See in 1, 2, 3 diradical system, we have studied that you can nicely see your hydrogen shifting, your studying methyl concept in this can you think about which can shifts.

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You can see bond migration I can migrate this bond that bond migration happens, you call as rearrangement product are something, but bond migration nicely happens, so write the structure will you do this type of thing just without seeing the board and writing the structure that will more interesting, write it by yourself without seeing board. So, you are getting one ring expansion one side and your getting a contraction one side, so you are getting type hexane and pentane system (No Audio From: 41.14 to 41.56).

And this reaction goes so nice, like it is very hard to do in other way just by a shining like, you get this product nicely, very good migration happens.

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Which bond?

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This one, the other one is

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This

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No what bond you are talking about, this one

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In this way, you want to

(())

Move this bond

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You think, one think you are saying here, if this bond I can move it is type of cyclohexane where you bicyclist system, where that bond you can always move see you have to draw like this then you will understand rather than drawing a cycle it never looks like cyclic system, then you will know how far that bond to move it up.

Just what you do is that, just draw moving this bond and see what product it and see always I am saying do not close your mind these are products we are getting, you do not close your mind if you have any option draw it and then show it to me, then we will discuss why it is not going, but initially itself do not say that no, draw the product if you have any other option draw it.

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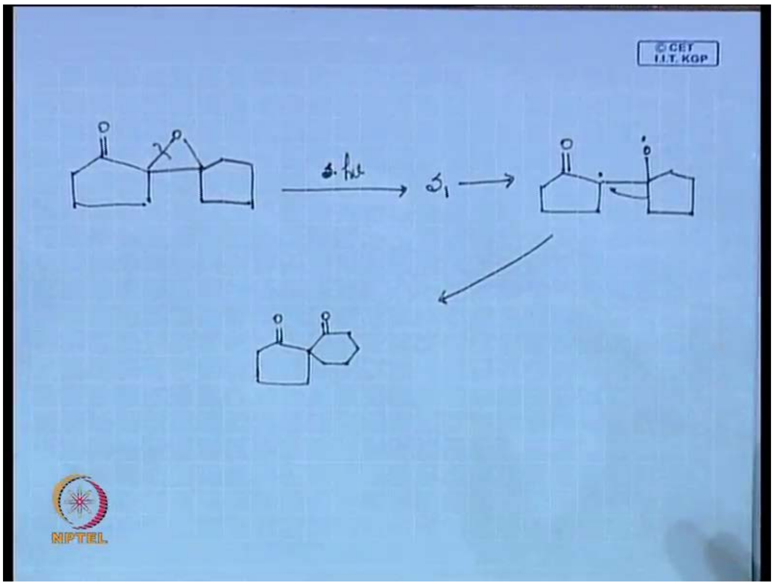

You take another example, I once shine light I might end up with my S 1 that is very clear, then you have chance of breaking a bond correct what is your alpha have an alpha beta, so you can take break this point fine, so you get system, you will get this (No Audio From: 43.58 to 44.26). Now, write the product you get a, I can move this bond to the radical this can happen six member suppose, six member see right see these are examples which you have to learn, you will see how different see just taking one example and doing a beta cleavage reactions not beta cleavage reaction have to know like what radicals we are getting, then if it is then you have to think about it most of time in beta cleavage you are getting only 1, 3 diradical, then you think what are the options in 1, 3 diradical (No Audio From: 45.23 to 50.46).

Whether your hydrogen can be shifted or your methyl can be shifted or you can shift the bond, so you are now left with three options hydrogen shift or your methyl shift or your migration of bond, I never give you a beta cleavage reaction mean.

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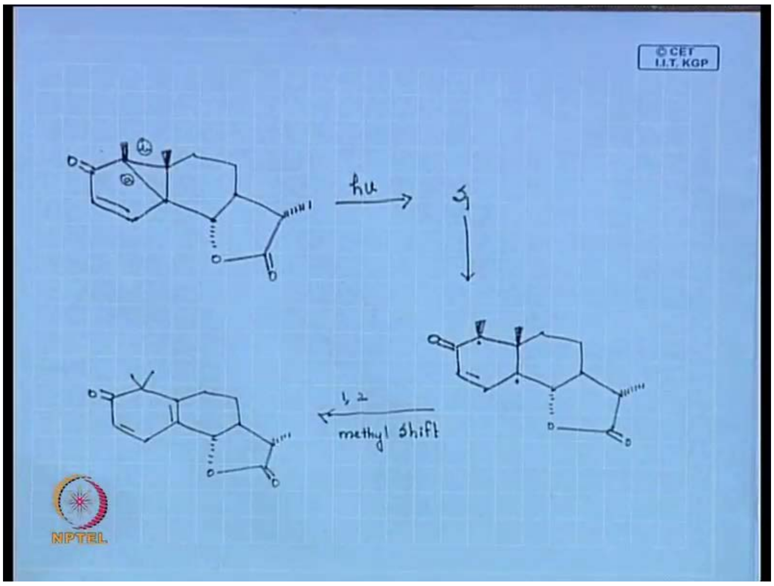

Now, I will take an example with singlet what happens like this is your famous example, actually I think you are seen this structure, just take our from like recollect from your mind where you have seen this structure, you have seen structure and you are going to deal with this structure in pericyclic reaction lot, right now we do not worry about that, part will see our whether what chemistry is going to happen in this case (No Audio From: 46.50 to 47.30).

So, have a system like this I ask you to shine like, you think about all the chemistry whatever you learn alpha, beta, 1, 5 1, 4 1, 3 diradical, see what you can think about and say that which will be the major product; once I shine like I get to my S 1, now say whether it will undergo and intersystem crossing to give me T 1 or it get me directly from S 1 how the system looks like, it like ketone which is an alpha beta ketone you know, and you have very strange type of ring, so can I do some chemistry from S 1 itself, it is possible, if I do from S 1 then what chemistry I can look for I can look for some beta cleavage right or alpha cleavage; in this case can I look for an alpha cleavage, how you can think of looking an alpha cleavage reaction I do not think, see if I give an alpha, just do if I do an alpha cleavage here it is not going to happen, if I do an alpha cleavage here again it is not going to happen, because I am putting a radical on a strain ring, so that is not going to be possible, so then I am left with choice of beta cleavage.

If it is beta cleavage then I have a cyclopropane ring, I can break this cyclopropane here, options are there I can break it here, where you want to properly break, this I can write alpha beta, I can write this also alpha beta, so I can I can call this A, I can call this B which ring you want to break.

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Because you have making to be free know you get a cyclopean, so that is how you looks to be once you know the idea it looks to be simple, so I will get a radical once I break this, so what you have now trying to do you want to it is a 1, 2, 3 you want to migrate a bond, hydrogen source available, what you, what this molecule (No Audio From: 50.10 to 50.38).

(())

Yes you can do your methyl shift nice, so that is how you ask yourself and say that this is not possible this is possible, so I do a methyl shift then, so this type of methyl shift is a now you have tell me like stereochemistry, where you can counsel your stereochemistry or you are going to lose your stereochemistry of your methyl shift want to counsel with, counsel (No Audio From: 51.18 to 51.45), it goes in a consistent fashion this all this, see your studied about your pericyclic reaction it does not go by pericyclic, it is consistent fashion.

It is it is you know that we are studying this this is a radical type of chemistry right, it is not consistent fashion, once your radical comes in, it is not going to be much more consistent. So, what happens then whenever you do, that is why when you do your triplet chemistry you lose your pericyclic you get non stereo specific product, but of you when you do with singlet yes you get stereo specific reacts so right same because, triplet or more like a radical clear.

I think these are the some good beta cleavage compounds, which can do beta cleavage nice fine, so in this class what we will do will finish up with a beta cleavage. Now, we finished our cleavage reactions, carbonyl cleavage reactions we have seen, we have seen completely alpha cleavage, we have seen beta cleavage, what I will do, next class I will give you some assignments on cleavage reactions so that you work it on and give the assignment. So, from next class we will start now hydrogen abstraction reactions clear, thank you.