Organic Photochemistry and Pericyclic Reactions

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Module No. # 01

Lecture No. # 21

Carbenes and Nitrenes

In the previous class, we were discussing about your singlet oxygen and the reactions right. So, in this class what we will do is that, we will see some important organic reactive intermediates, we will study some important organic reactive intermediates right. So, in this class we will understand some organic intermediates, their synthesis and their reactions and structures.

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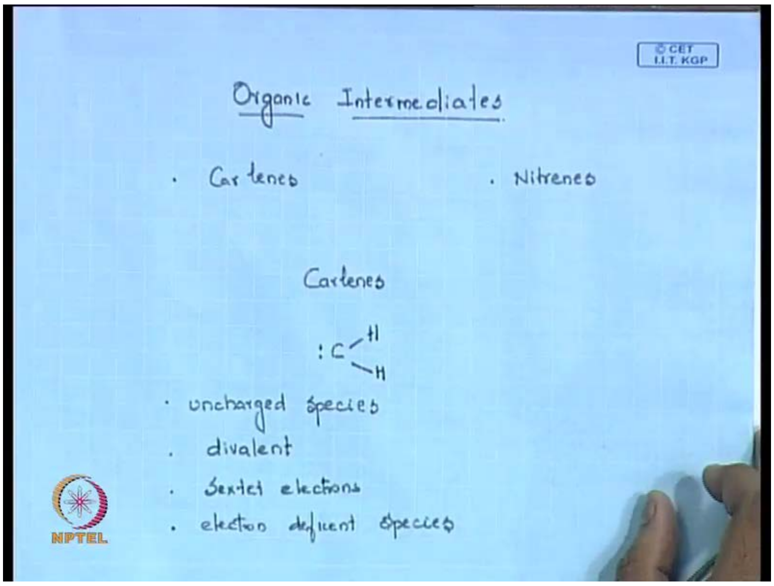

Organic Intermediates

- Carbenes
- Nitrenes

Carbenes

- uncharged species
- divalent
- Sextet electrons
- electron deficient species

So, basically I am going to deal with carbenes and the class of reactive intermediates is your nitrenes, so we will study carbenes as well as nitrenes. So, initially we will discuss about carbenes. So, you have you know about carbenes much, because you have studied in detail earlier, we will see from photochemistry point of view how we can understand carbenes.

This is your simplest carbene right, so that is your methylene right we call them as methylene or it is a simplest carbene, seeing this structure can we write some salient feature based on this structure, so what about your carbene now? Your carbene is type of neutral, right is a in carbene most of the time your carbene atom is neutral and you call them as, that is why, they are uncharged. First thing you can say it is an uncharged species.

The second thing you can seeing the structure you have can you guess anything? It is divalent, and you can say it is divalent right. Another thing you can say that, the central carbene atom is surrounded by sextet of electrons right just by the structure (( )) you saw central carbene is surrounded by sextet of electrons and it is and finally, you can say that it is an electron deficient species.

Just refreshing what you have studied earlier, so your carbenes, the central carbene atom it is neutral. So, it is more or less it is an uncharged species, it is a divalent and the central carbene is surrounded by your (()) electrons, so sextet electrons and it is a type of an electron deficient species.

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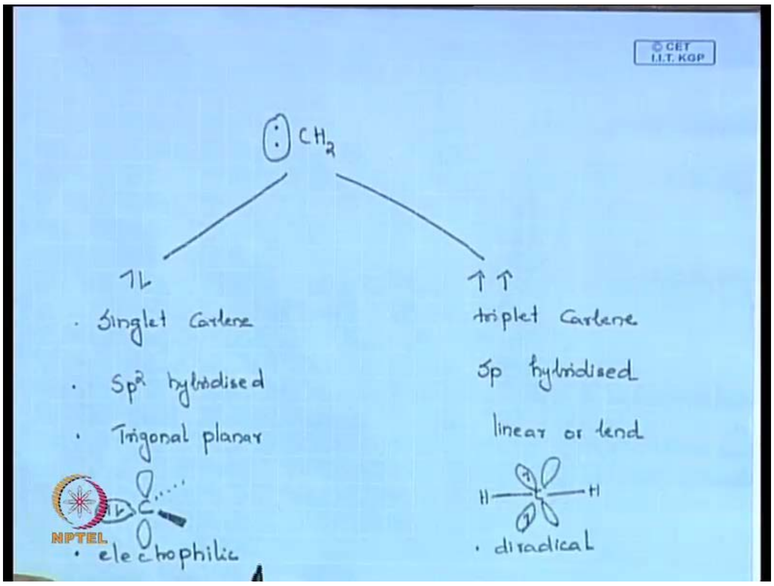

Now, coming to these two electrons, now if I introduce spin, I will just put like two dots there, if I write it in the spin then, there is two ways I can write the spin, because these are more like a p orbital right. So, I can write this spin in two ways; one, I can write this spin in this direction or I can write this spin like this right generally. So, what is this one?

So, it should be because, we know that if it is paired we call it as singlet and if it is we call it as triplet, so we call we call them as a singlet carbene, we can call this as a triplet carbene.

If you see their hybridization if it is in singlet, it is how it will be in the p orbital, if it is what hybridization it takes place, S P 2. So, you have a S p 2 hybridized in singlet, in triplet it should be S p hybridized. So, if it S p 2 hybridized then, what should be the structure, it should be trigonal planar and this should be if it is S p most of the time your carbene is linear, there are cases where it is bend also, but linear you can see most of the time. If you want to draw their structures of carbene you can write this way 2 P S trigonal planar. For linear, I can think of (No Audio from 06:17 to 06:29) I can write like this to be linear. So, singlet carbene is S p 2 hybridized trigonal planar, triplet is S p hybridized and linear or bend this is about their structure right. So, the structure we now we know it is trigonal planar and another is linear any reactivity point of view.

How this should be, how this should be, triplet should be but, how they react nature, whether this nucleophilic or so, singlet is electrophilic right and your triplet is, it is a diradical. So, that is how you can at least view your triplet as singlets, singlet is more like an electrophilic, most of the reactions works like electrophilic, triplet you work with your radical chemistry the rare cases, but their character is more like an electrophilic. Now, we will what we will do is that, we will take individual singlet carbene and see its synthesis how we can generate rather than synthesis we call it them how we generate singlet carbene, then how singlet carbene does reaction, then we will say triplet carbene how we can generate, how we can see do the how it does a chemical reactions.

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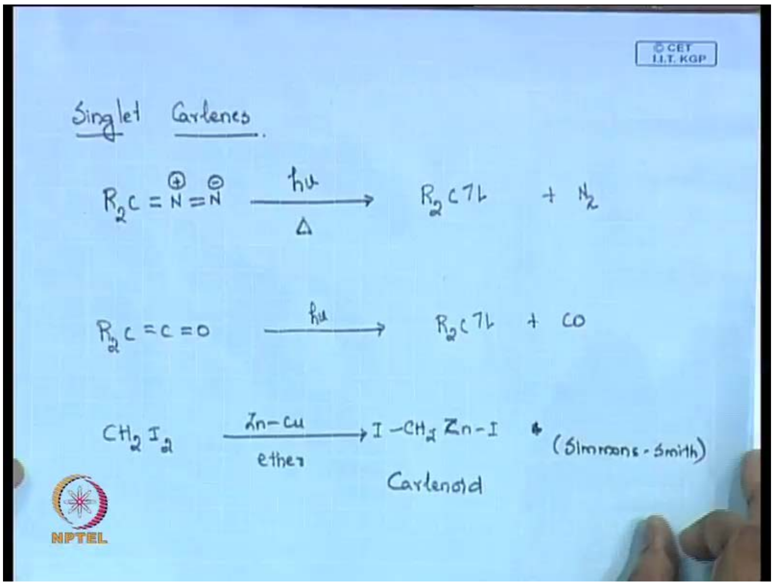

So, we will start with singlet now (No Audio from 08:31 to 08:46), any idea how we can generate singlet carbene, general general synthesis, which component you like to use, yes you can take your diazo compounds right (No Audio from 09:11 to 09:21) take your diazo compound you can fertilize or you can even thermalize, if you heat also it works.

So, you end up with singlet carbene plus nitrogen I hope that, you have studied all these things just we want to refresh it back. So, you get it idea, any other synthesis which you will think, from ketene you can synthesize right again you can take a ketene you fertilize them, so you get your singlet carbene. There is one reaction which you have studied in your bachelors, name reaction, but it is not exactly carbene, but you have studied that what is that? Regularly you use that, Simmons-Smith reagent right. So, what is about that Simmons–Smith, you take a C H 2 I 2, then what reagent it is, yes you take zinc copper, ether. So, one thing here, it has one difference is zinc halide, zinc halide.

What you call this particular one, it is a carbenoid that is why I want to recollect you that, it is not exactly carbene, it is a carbenoid we call it as a carbenoid; it works generally like carbene; all its reactions and everything is more like carbene, but once you go to its selectivity you can differentiate this from carbene this is Simmons-Smith this three, but majorly these two one you use normally you take regularly, if you use in lab you take diazo methane, you fertilize and end up with a singlet carbene, nothing odd reaction, it is a very simple one, ketene also you can do, it works fine, but this one is more like a carbenoid not like carbene chemistry.

(( ))

Dichlorocarbene is also carbene, it is not that you see I am just making this R, it can be anything.

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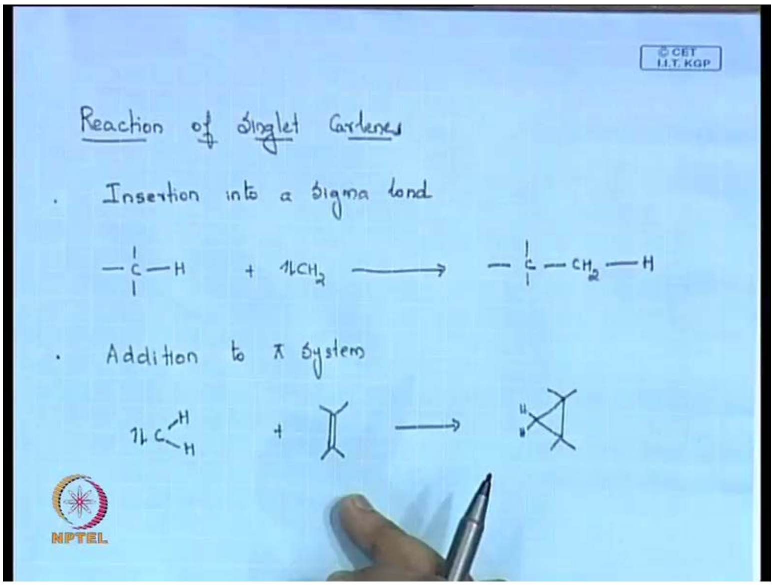

Reaction of Singlet Carbenes

- Insertion into a sigma bond
- Addition to π System

Now, we will see the reactions of singlet carbene. So, that is how you can generate them (No Audio from 12:19 to 12:41), reactions singlet carbenes which is very good reactions we choose.

(( ))

That is addition to alkenes that is there, but more than that you have not seen other chemistry does, other species this does very fast reaction.

(( ))

Insertion into a sigma bond very characteristic feature of your carbene, if you have a system like have an alkane, where I cannot do anything, if you can by any chance if you can by means you can generate this singlet carbene, it nicely gets inserted into this sigma bond. So, you will end up like C H very nice chemistry of singlet carbene and it does very fast. Only problem with singlet carbene insertion is that, it is very random, there is no much selectivity there, if you have like secondary, tertiary or primary, it inserts randomly, there is no selectivity it has that point you should remember, when you talk about insertion into a sigma bond, why I am saying that, when I go to nitrene, singlet nitrene does this reaction much more selectively, but carbene does not do that, it just randomly inserts into C H 1, it has no big selectivity that is the first point you have to remember. The second reaction as you said, it is addition to a pi system, a singlet carbene with alkene see I am not discussing anything right now about the stereo chemistry, when I go to triplet carbene I will discuss about stereo chemistry right now you just think that, singlet carbene can add to a pi system, it nicely forms a cyclopropane, it is very stereospecific where I will discuss when I talk about triplet carbene that is another secondary reaction.

So, these are very common insertion into a sigma bond and addition to pi system, why insertion to sigma bond is much more used like nitrene it is used a lot, it is very famous insertion into a sigma bond, why? Any idea, that that reaction has become like very catchy now a days, because you can insert into peptides you have a peptide you want to insert a end connected some flouro pole, which is nitrogen then, you can take a peptide generate a single nitrene or it just inserts into a peptide and the peptide becomes flouro pole, it becomes fluorescent, then you can watch what happens to the peptide, how it interacts with the cell and everything. So, that is why that insertion has become very catchier now a day, which you do much in nitrenes.

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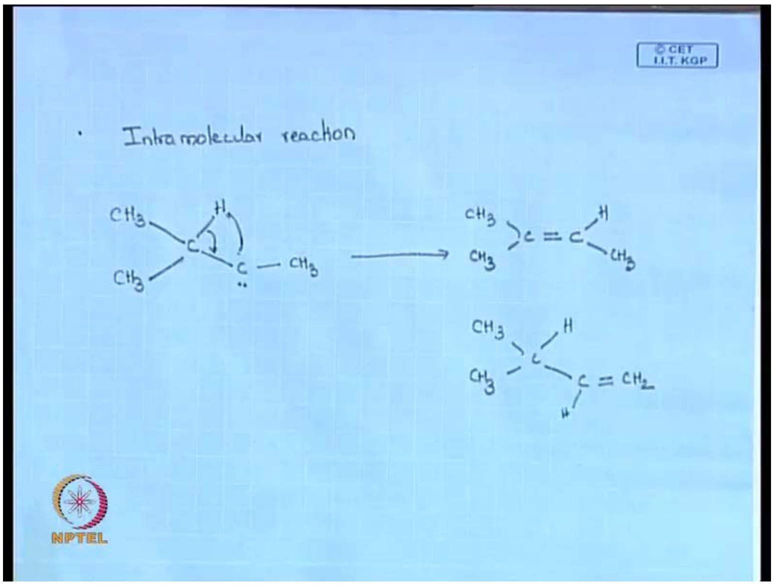

Then, any other reactions you can see this intra molecular which happens like for example, I have C H 3 you can call this as hydrogen shift or you can call this as intra molecular you have heard this one I have generated a carbene here, what do you can think it can do, any idea what it can do I have a carbene here which you have studied in most of your chemistry, it nicely takes this hydrogen this one two hydrogen shifts all these things you can see rearrangement reactions all these things you can see. So, this hydrogen moves across this I take this hydrogen out, somewhere and (( )) like this.

So, you will end up with C H 3 you can do this or you can take this hydrogen also that is also (( )) that also you get product C H 3, C H 3 you can get this also, thus nice one two hydrogen shifts you call as intra molecular reactions.

(( ))

Because this is singlet I can push my two electrons to pick this hydrogen out, then I can push this double bond to make an alkene, it is not triplet, it is singlet, triplet also it happens, triplets also does nice hydrogen abstraction reactions, but that is mechanism is different, any other reactions a my other reactions, which you can remember carbene does, because this three you have studied, you have studied insertion to C-H bond and you have studied addition to pi system, intra molecular reactions any other which you have studied.

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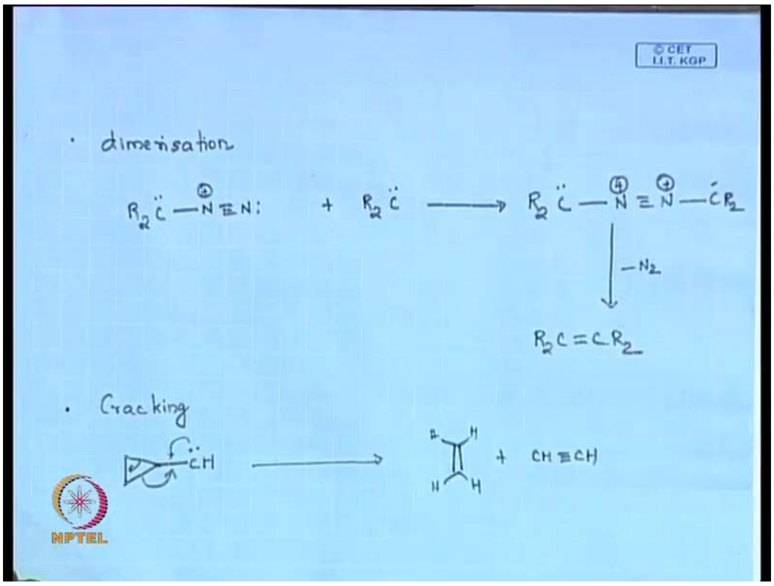

I have studied dimerisation; carbene does nice dimerisation reactions also like for example, if I take an azo compound, type of azo compound. Based on the same azo compound I have generated a carbene, R 2 C dot. So, I have generated a carbene using the same compound and this and this carbene waits till it sees another molecule, it forms a, get this and this nitrogen goes off giving this reaction product that also carbene does. See, this type of chemistry when you can think about when there is no hydrogen source, when you are doing fertilizes and that fertilizes does not have any hydrogen source. For example, I am doing this chemistry in benzene, then it does not do anything, there is no chance of hydrogen abstraction or anything, insertion into sigma bond then, it does this hybridization reaction.

Now, recently people are using this carbene chemistry, where in petrol industry for cracking's, studied that cracking purpose. See, if I want to crack this, break this into what I am going to do is, just going to generate a carbene, what it can do.

(( ))

What sir I am missing some. So, you can easily (( )). So, I can get my I can get my (( )) plus this type of cracking's now a days are started, because you just have to generate carbene that is all. Because cracking you know cracking by what advantage you get, you get lot of heat, because you can think about fuel and all these things slowly started of this chemistry cracking reactions.

One more interesting reaction is there what that, carbene which I have left, yes sir one more reaction which I have left, synthetic use it has lot of synthetic application.

(( ))

Methylation yes you have that addition you can do methylation, but that is addition is to pi system you can talk about.

(( ))

That you can think about another one, you can make this ylides, because you know ylides synthetic utility is so high. You have studied about ylides you know sulphur ylides, phosphorus ylides and all this and after making ylides you can do n number of products that you can do with carbenes.

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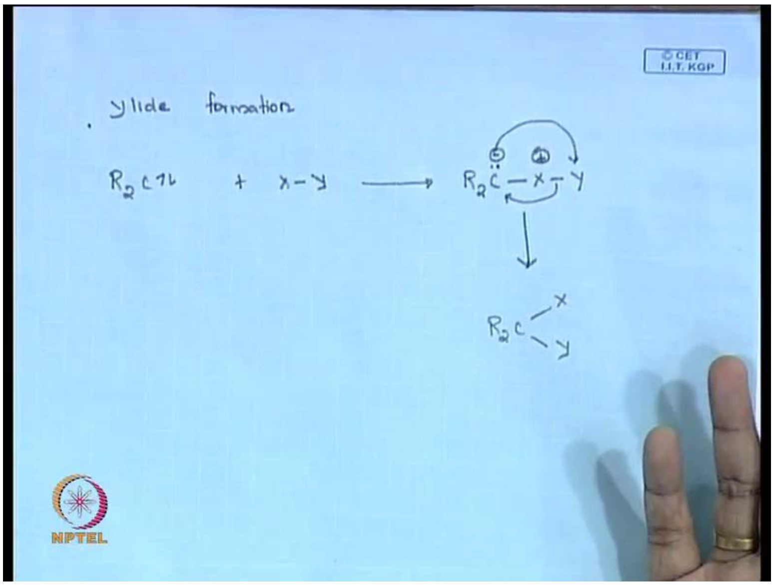

So, if I singlet carbene I have just example I have take X and Y. I can think of my carbene this, this we can make, it is a type of an ylides, then I can push this Y, R 2 C X and Y this normally you can do, this type of ylides, slowly started up during this chemistry. See, normally which few study is basically three important reactions you study on carbenes, which you can remember; one, is your insertion in to sigma bond another is your addition to pi system, then dimerisation reactions, these are very common in carbene, if you take carbene reactions this happens very fast that should be your in mind this three reactions. Then, how to synthesize them, take diazo methane you get singlet carbene or you can even take carbenes, is a key sorry ketone you can get your carbenes this is more about singlet carbene carbene.

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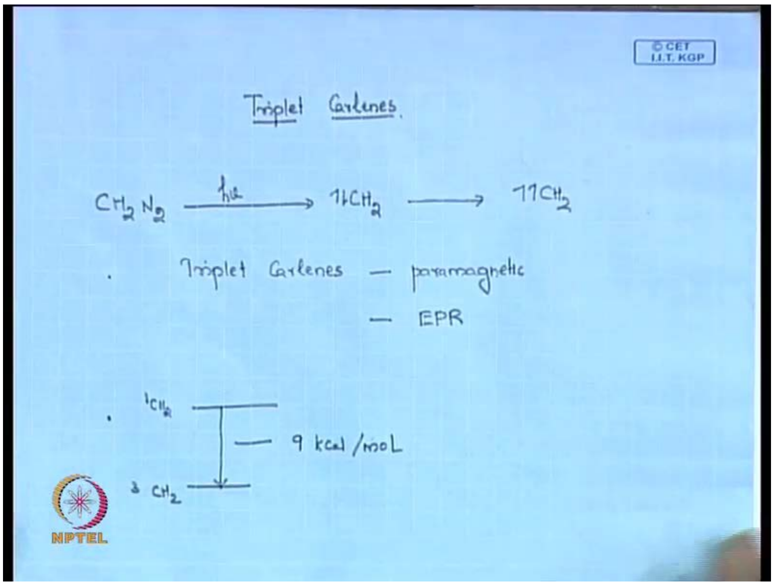

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Triplet Carbenes.

$CH_2N_2 \xrightarrow{h\nu} {}^{\uparrow\downarrow}CH_2 \longrightarrow {}^{\uparrow\uparrow}CH_2$

- Triplet Carbenes — paramagnetic
  — EPR
- ${}^1CH_2$ — 9 kcal/mol ${}^3CH_2$

Now, we will go and see what happens with triplet, how you can generate triplet carbenes?

(( ))

fertilizes on an (( )) very good that is a very good thing then, that is a very good fertilizes on on inert conditions we can do that, if you take see for example, I am taking a diazo meter and if I fertilize you know that definitely you will end up with the singlet, but if your (( )) is inert like you are doing this in argon atmosphere and that is one. And if you can do it in low temperature then, that is also possible. Then, if you try to do in gaseous phase, you do it in low pressure also, if you have all this criteria you can make your triplet carbene. So, there are many criteria you can do it in inert, you can do it in low temperature, low pressure, gaseous phase you all get your triplet carbene.

Any direct evidence that you say that, I got triplet carbene I ask you to go to the lab make you to (( )) carbene and you can say that, I have made triplet carbene how, direct evidence I am not doing I do not want you to know one more reaction directly sir I have made triplet carbene.

(( ))

That is again doing a reaction right, any direct evidence you can think about. So, triplet carbenes are what, how they look like triplet carbenes?

(( ))

Diradical or anything, I want one more word on that, triplet carbenes are paramagnetic right, if this paramagnetic then you know that, you can do by EPR you can observe them in EPR will be directive evidence. What is the advantage see, if I can make a stable triplet carbene or stable triplet nitrene for example, can you think any advantage it has, if I can make a stable triplet carbene, carbene which can be stable for at least six months triplet carbene in solid state.

You think can we do any application across that, that is why lot of work is done on stabilization of carbene, which I am not going to deal with, which you have studied, you can stabilize carbene by resonance effect and substituent effects and all these things. If I make a carbene stable particularly, triplet carbene stable, what what advantage I can say?

(( ))

That is reaction point see triplet carbene is paramagnetic; it is highly, it is organic magnets, it is a very good organic magnet you have seen organic magnets. See, advantage of organic magnets, because this will be magnet, if it is stable for six months or whatever it will be a very god magnet.

And organic magnets are light, they are highly flexible, then I can design some screens say if you see this type of screens say if you see this type of screens in TV's, they more are like flat, they are not flexible. If you can think about an organic magnet for which can sustain for a longer time, then you can think about a screen which can be even flexible, it does not need to be flat all the time, it can be flexible also then, you can have your TV in your hand like a watch.

So, that is why lot of work has been right now is working on triplet nitrenes and triplet carbenes particularly to make them stable for longer time. Only problem is that their stability. So, you can make them stable for at least six years or whatever, it is in many ways, then you are ending up with a very good organic magnet, which you can think about in making chips and electronic device and all these things. So, that advantage this has right.

The second part is that, why the singlet carbene just undergoes sort of inter system processing to triplet carbene. Normally if you see, this is triplet and this is singlet, this energy gap from singlet to triplet is more or less very small that is 9 kilo calories per mole that is all (Refer Slide Time: 30:18). So, that is why in low temperatures it just moves down (( )), the energy gap is very small even there are cases, where it is 6 kilo calories per mole, so its range between 6 to 9 kilo calories per mole. So, you can always push your carbenes from your singlet to triplet.

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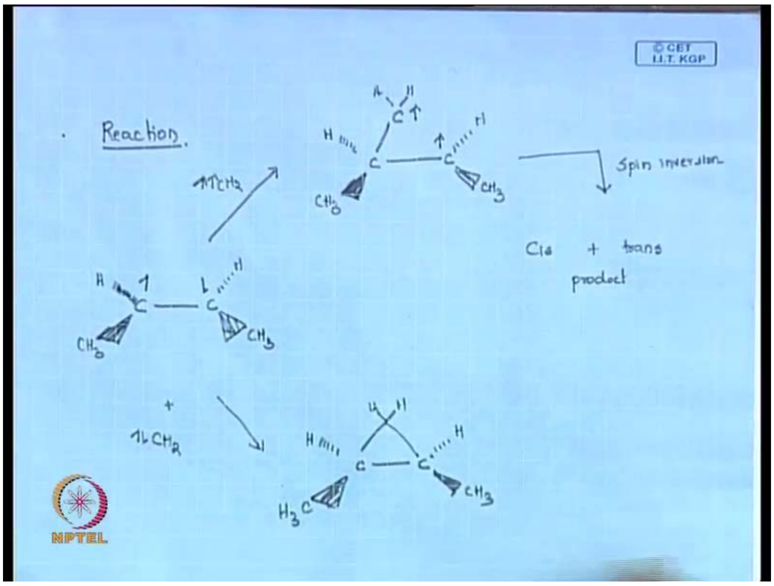

So, that is synthesis generation of triplet carbene, then we can see the reaction we will discuss this particular reaction that is I have an (No Audio from 31:13 to 31:32) just for example, I have a system in carbene like this. So, I can just (( )) add this, it will be a very (( )) process I can just add to this and I can add to this. So, my reactions will be stereospecific right, because there is no it is a very (( )) process this to this and this to this or you can push your 2 electrons or push it back that is also you can do, so it is highly (( )) process.

So, your stereo chemistry is most of the time it is preserved, what carbene is this?

Singlet.

See, any where people will ask this question most of the time. If, I have a triplet so what happens, if it is a triplet then, (No Audio from 33:00 to 33:25) I will end up like this right you can put it to other way round also, but both the spin will be same, it can be like this or it can be like this, but spin will be most of the time same. So, now what happens so you get a proper spin inversion followed by rotation. So, your whole stereo chemistry is now lost; now you end up with both cis and trans you can get both cis plus trans, that is very important about singlet and triplet, that is how you know its one going by radical chemistry and another going by more like an electrophilic.

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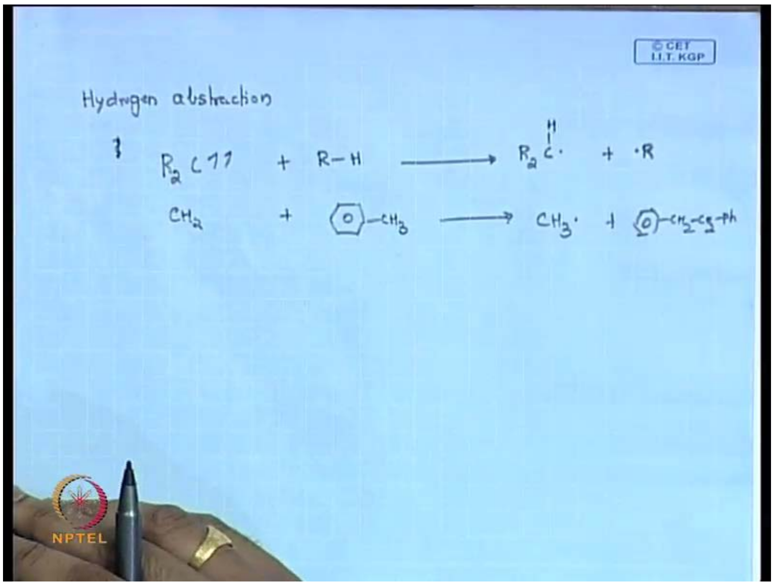

One more reaction, which triplet carbene does which you should know it is a simple, it is called hydrogen abstraction (No Audio from 34:46 to 35:06) can be like this just see, you can get H here and dot here plus end up R dot, this reaction is little bit important once like you should know see, if I have take see for example, same like C H 2 into (( )) see hydrogen extraction process is little bit hard, it needs a very good lifetime for a molecule to go abstract an hydrogen.

See, that is what that is the very important thing that tells you like you can stabilize singlet carbenes see singlet carbenes lifetime is very fast, once you generate singlet carbene it reacts like this. So, it is a, it is not a long live intermediate, but if you think about triplet carbenes, they are long lived intermediates, because these are the reactions this tells that it is a long lived because, it stays in the solution it finds the counterpart and it has to abstract an hydrogen. So, if you does that you will end up with, you will end up with type of bi benzene which you can see lot, very important reaction which your singlet carbene never does, it all depends upon the lifetime, it has to stay in the solution to pick that hydrogen it does (( )). So, these are the two important reactions of triplet carbenes which you have to remember. Now, so that is all about carbenes.

So, carbenes you have seen about singlet carbenes and we have seen triplet carbenes, their reactions and how they are generation. We will see now another important intermediate which is your nitrenes, which you have not studied much.

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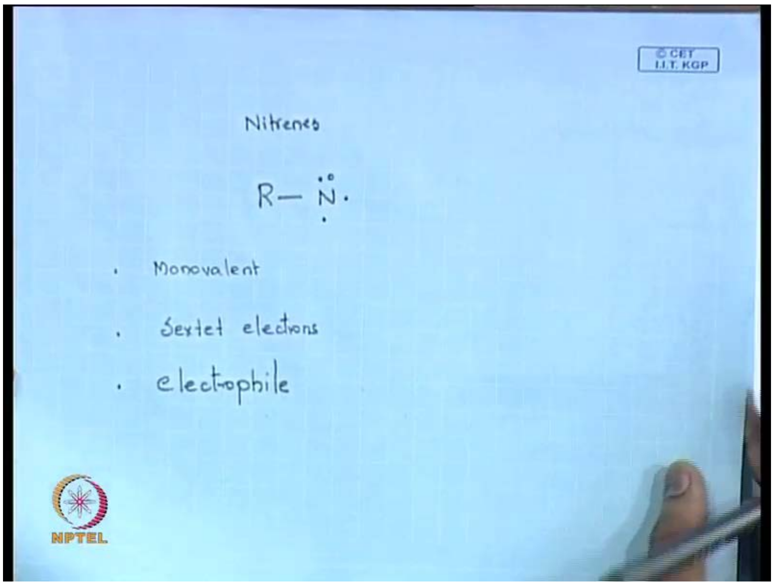

Nitrenes

$R-\underset{\cdot}{\ddot{N}}\cdot$

- Monovalent
- Sextet electrons
- electrophile

So, if I draw the simplest structure of nitrene it should look like this right. So, carbene was carbene is a divalent. So, this is monovalent right, there is only one, so is a monovalent. That is divalent, carbene just you have to compare when you talk carbene and nitrene right same way this is surrounded by by sextet electrons. So, whether this like carbene in carbene, carbene was neutral this is charge type of charge right and it is more and nitrene becomes more like an electrophile whenever you study nitrene compare it with carbene, tells you much.

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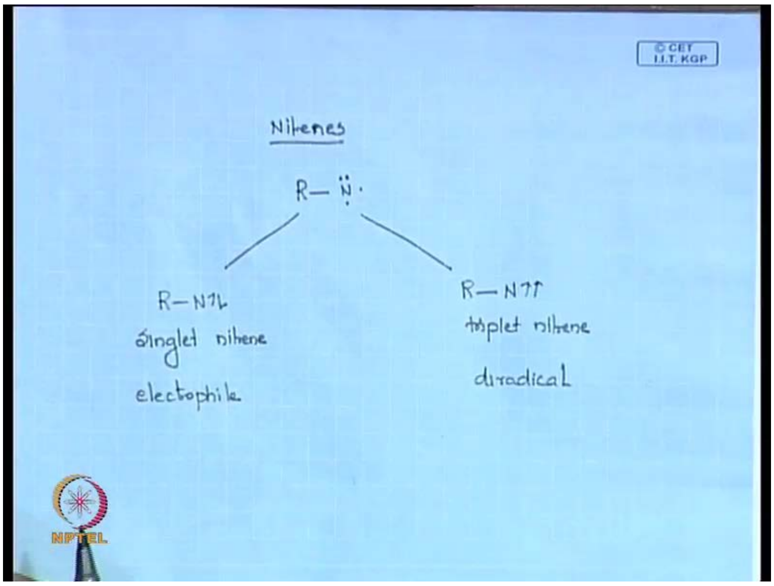

Nitrenes

$R-\ddot{N}\cdot$

$R-N\uparrow\downarrow$

singlet nitrene

electrophile

$R-N\uparrow\uparrow$

triplet nitrene

diradical

So, again I have that two electrons based on the spin of this electrons I can again divide nitrenes into two, one I call them as, so this is your singlet nitrene, this is your triplet. And again this will be your working like electrophile and this will be diradical and most of the case nitrenes are linear, not like your carbenes; carbenes has sometimes gets this trigonal planar, but nitrenes know most of the case they are linear in shape most of your nitrenes are linear. So, there is not big difference between triplet and singlet, so most of the time they are in linear.

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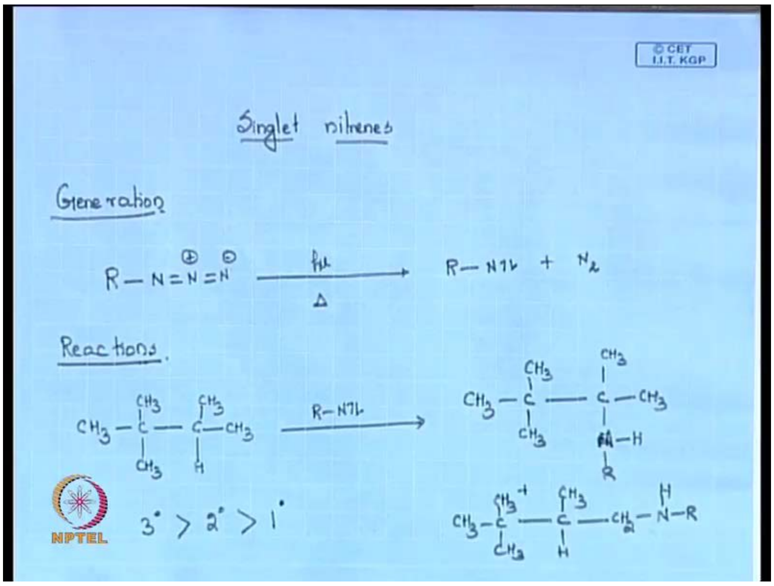

Singlet nitrenes

Generation

$$R-N=\overset{\oplus}{N}=\overset{\ominus}{N} \xrightarrow[\Delta]{h\nu} R-N\uparrow\downarrow + N_2$$

Reactions.

So, we will now get into singlet nitrene now and see how singlet nitrene works, any idea how to generate singlet nitrene, how you can generate singlet nitrene anyone, come on man how you will generate singlet carbene you take a type of azo compound, because that nitrogen goes off based on that idea you generate a singlet carbene right. So, in this case if you want to remove two nitrogen out and you want to generate a nitrene, what you want to do? So, it should be a compound which has three nitrogen's, so what you get?

(( ))

That is all you take an azide you heat it or you thermalize or you fertilize you end up with a singlet nitrene (No Audio from 41:28 to 41:48) this is one very good method, there are I have seen like this is the only best method by which you can generate triplet nitrene, there are some other methods, but this is the best one, because making azide is easy how do you make a azide, if I want to make an azide like I want to make like some azide like benzyl azide, you just take a benzyl bromide add sodium azide just room temperature stirring and you get nice. So, how you know you have got azide, any spectroscopy evidence?

(( ))

IR, where it comes, azide as I tell it is a very distinct speak 2 1 0 0 and it will be just like your carbeneate like it will be stretching will be so huge, it will not be like a small peak it will be a very huge peak. So, IR is the best way to say that, you get an azide and this reaction goes like 90 to 95 percent, it does not even want to do column, then you can fertilize them you get a nitrene.

So, if you see the reactions of this nitrene, singlet nitrene I am taking this type of (No Audio from 43:18 to 43:34) see what happens in singlet carbene if I generate a singlet carbene, it undergoes insertion in to sigma bond right. So, triplet nitrene also does the same thing sorry singlet nitrene also does the same thing, insertion to sigma bond, but it is much more selective. For example, I get this as the major product C H 3, C nitrogen N H R, nitrogen this is N and I might get this also little bit, that is how your peptide you can insert your nitrenes into your peptides. See, if I take a nitrene instead of my R, if it is for example, (( )) or like (( )) are highly fluorescent.

So, I can make my (( )) nitrene singlet nitrene, then if I react with my peptide, it can easily insert into my peptides like basically proteins. If, you want to insert into a protein you can insert it, then what happens my whole protein will be fluorescent, and then I can visualize by fluorescent microscope, how this interacts and I can start studying the that is called the fluorescent imaging.

So, this nitrene has a big role in fluorescent imaging you can you can that is a big field like fluorescent probes, fluorescent imaging chemistry and all where you can directly visualize what is happening with your cellular level. But, in this case if you say this is your major product, the secondary one and your primary one is very like very minor amount. So, it has some selective not like your singlet carbene, singlet carbene randomly does. So, singlet nitrene is not that, it has some selectivity. So, 3 degree first, it does gives a major product with 3 degree, then it goes to 2 degree and then your 1 degree comes here.

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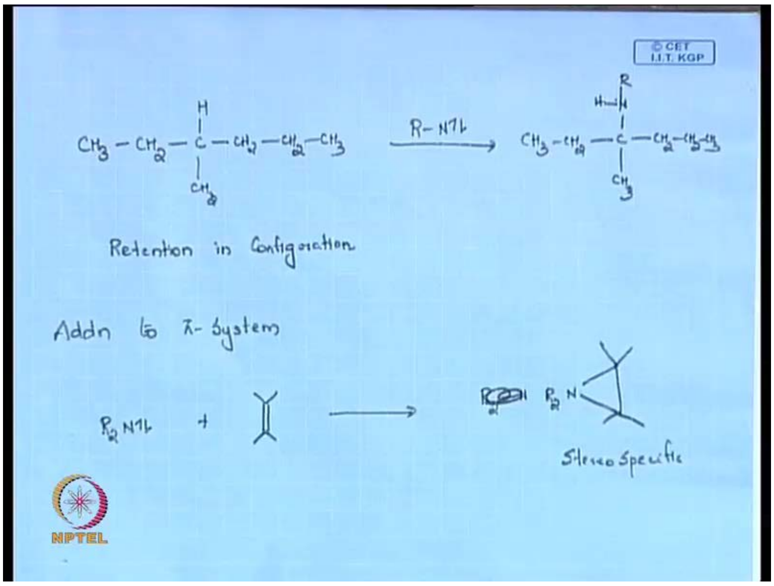

Another thing also you should know in the insertion particularly, with the nitrene that also you can see in carbene also (No Audio from 46:18 to 46:29), take a type of chiral carbene and does this, you know that it goes only to triplet 3 degree (( )). So, what happens in this case is that, you get retention in configuration. Singlet also it gives singlet carbene also gives retention in configuration, but only it is random; triplet, you can see very selective and retention in configuration and singlet nitrene.

Then, this part you know there is nothing need to talk like this, addition to pi system you know now, that singlet will give you stereospecific product, what is this molecule which I get now after the reaction, aziridine right aziridines are you know about aziridines right they are very important for agro chemicals and they have lot of activities aziridines it is easy to make you take an alkene you generate your singlet nitrene you end up with your aziridines, azirines are what azirine, aziridine is this, azirine is if you have a double bond, you get stereospecific that you know. Now, we will just slowly go to that is all about your singlet nitrenes.

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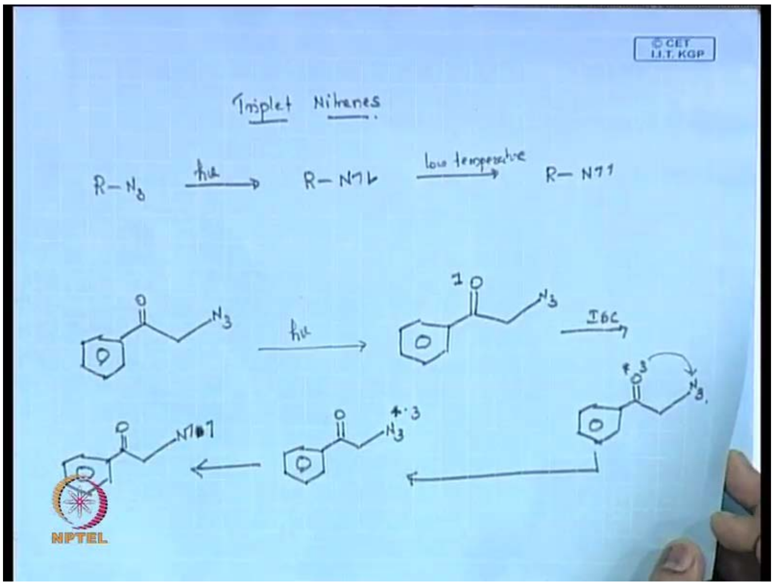

Triplet nitrenes just as you said, once I fertilize I get my singlet and this in low temperature just like your carbene gets you triplet. Any other way you can think that, if I can you generate triplet nitrene can you think any other chemistry, I want to completely bypass this singlet nitrene. See, whenever you say it is low temperature you have intersystem crossing singlet, then it always will be in equilibrium most of the time you will have singlet as well as triplet.

I want to completely bypass my singlet nitrene I want to get only triplet you have studied this just want that whether you can use it (No Audio from 50:07 to 50:15), no. See, I take a system like this for example, I take this I fertilize now, but I fertilize in such a way that, see azide have absorption round about 250, 270 that is all. So, I fertilize in your test tube, so test tube is normally (( )) your (( )) test tube. So, their cut off is how much regular test tube, they have starting from 290, but exactly 310 nano meter. So, what will happen if I shine light now on this compound in my test tube I take this compound and shine light in test tube what you have what will happen, my azide will not absorb any light, so whatever light will be absorbed by my ketone. So, what do you know about ketone, once the ketone absorbs the light what happens to ketone it goes to, come on man, it goes to singlet right, then it undergoes a nice intersystem crossing to give me get my triplet.

Then you know that, there will be an energy transfer can always happen right. So, this can do a energy transfer, which you have studied you can have an intra molecular energy transfer. So, it does a nice energy transfer to give me what, so if it because, it is triplet azide right now, it will be in the triplet state. So, that will give me a triplet nitrene.

So, I can completely bypass now my singlet right this is very interesting process, this is how you can generate, these are the two ways; one, you can (( )) directly your nitrene singlet nitrene, low temperature you can go to triplet or you can use your energy transfer concept.

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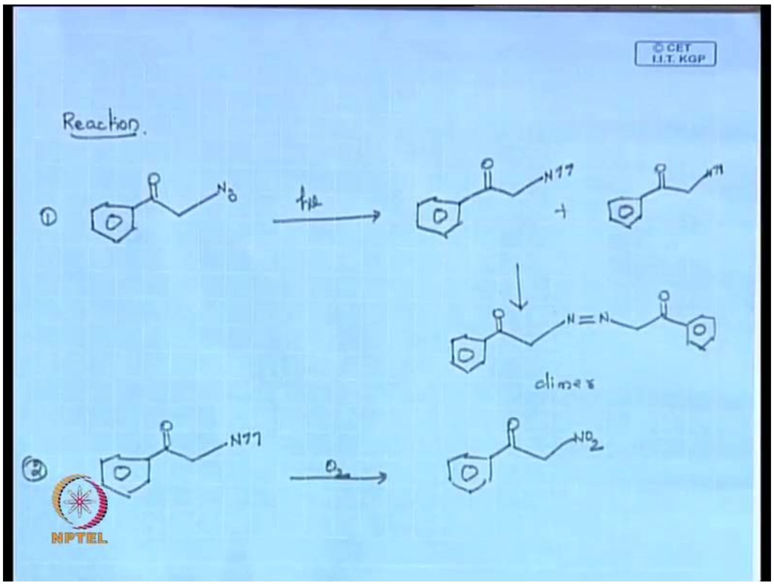

Reactions of triplet nitrene for example, I am taking this compound fertilizing this, it gets me a triplet nitrene, this triplet nitrene reacts with another molecule of triplet nitrene to give me dimer (No Audio from 53:49 to 54:01) this type of dimer you can get. Another important reaction triplet nitrene does any guess, if I treat it with oxygen what will happen, because oxygen is triplet in ground state and my nitrene is also triplet. So, they can react. So, you end up with nitro compounds, there are many nitro compounds made easy to make nitro compounds like this way, you make chloride from chloride you just use sodium azide then become nitro and from azide and azide with your oxygen end up with your nitro compound right, these are the two main reactions of triplet nitrenes.

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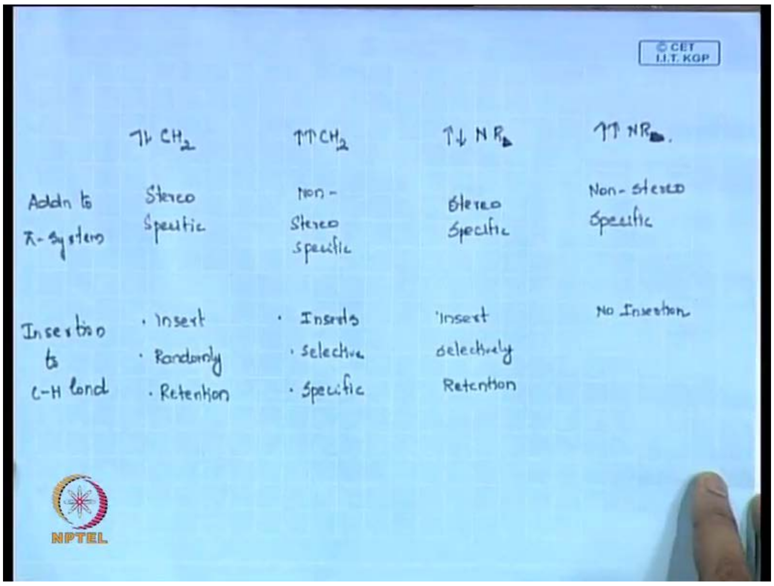

	$\uparrow\downarrow CH_2$	$\uparrow\uparrow CH_2$	$\uparrow\downarrow NR$	$\uparrow\uparrow NR$.
Addn to π-system	Stereo Specific	Non-Stereo specific	Stereo Specific	Non-stereo Specific
Insertion to C-H bond	· Insert · Randomly · Retention	· Inserts · Selective · Specific	Insert selectively Retention	No Insertion

I will just now a sort of summarize these nitrenes, just two reactions; this is my singlet carbene, triplet carbene, singlet nitrene, triplet nitrene sorry sorry. So, we will see addition to pi system how this (( )) work, what happens with singlet carbene addition to pi system you have studied that, it should be.

(( ))

It should be stereospecific, this should be non-stereospecific, again this should be stereospecific and this should be non-stereospecific.

This is the important part you should know, insertion to C-H bond how it works? Singlet carbene can insert, but they insert randomly you can see little bit retention. There, triplet carbene inserts, but not that much you can see selectivity as well as specificity, it will be selective it will be specific. Singlet nitrene, it can insert, but it will insert selectively and it also does retention. Triplet, no insertion you cannot see any insertion there. So, that is all major about your organic reaction (( )) these are the two, which you had studied carbenes and nitrenes most of the time, thanks.