Reactive Intermediates: Carbene and Nitrene

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Lecture – 07
Reaction of Carbene

Hello, everybody. Welcome to the lecture of Reactive Intermediates Carbene and Nitrene. So, today we will learn the Reactions of Carbene. So, before this topic what we have studied; we have studied the introductions of these carbenes and after that their structure and then we have studied how the carbenes can be generated by various methods.

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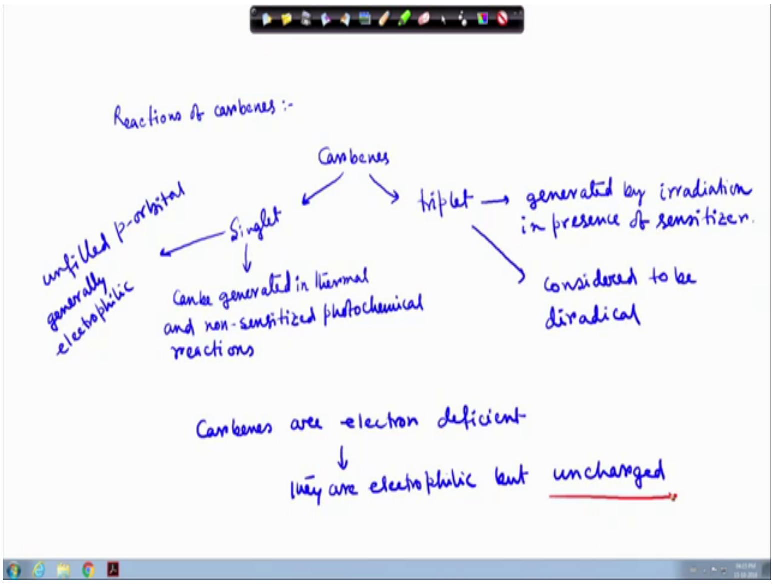

Reactions of carbenes :-

Carbenes

Singlet

unfilled p-orbital
generally electrophilic

Can be generated in thermal and non-sensitized photochemical reactions

triplet → generated by irradiation in presence of sensitizer.

considered to be diradical

Carbenes are electron deficient
↓
they are electrophilic but uncharged

So now, today we will learn the reactions of ok so, this is reactions of carbenes. Now, if we want to know the reaction of carbenes as already we have studied there are two type of carbenes. One is singlet another one is called triplet, ok. So, we have to studied the reactions of two different type of carbenes, right. So, now, in general it can be generated those singlet carbenes can be generated in thermal and non-sensitized photochemical reactions. So, how they can be generated? They can be generated singlet can be generated this can be generated in general in thermal and non-sensitized photochemical processes, whereas this triplet us these can be generated by irradiations in presence of sensitizer, fine.

So, basically once we can generate these type of carbenes, now they can do various type of reactions. So, how they will react in principle singlet carbenes they have these unfilled p-orbital. So, what they have these singlet carbenes they have these unfilled p-orbital. So, if it is having unfilled p-orbital, so, definitely it can accept electrons. So, in general they can react in electrophilic manner. So, generally electrophilic, fine ok, but in case of triplet carbenes as these two electrons they are not paired, they are actually staying in one s p 2 as well as in p-orbitals. So, in that case it can be considered to be diradical, ok.

So, from here we can suggest that definitely the reactivity of these two carbenes are different. So, their reactions will be different. So, in generals what we have learnt that carbenes are electron deficient fine, ok. So, they are electrophilic. Obviously, in absence of the strong resonance interactions like what we have found in case of these anisotropic carbenes it is not like that. So, in general they are electrophilic. So, they are electrophilic ok. Obviously in absence of strong resonance interactions, but uncharged it is this is very important that this is uncharged, fine.

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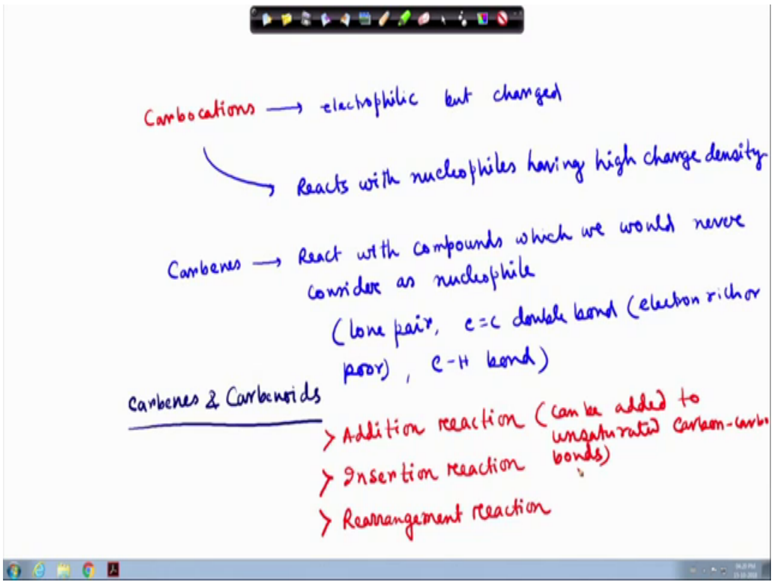

Carbocations → electrophilic but charged

→ Reacts with nucleophiles having high charge density

Carbenes → React with compounds which we would never consider as nucleophile

(lone pair, C=C double bond (electron rich or poor), C-H bond)

Carbenes & Carbenoids

- Addition reaction (can be added to unsaturated carbon-carb bonds)
- Insertion reaction
- Rearrangement reaction

So, once it becomes the uncharged then they will react in a different manner. If you say that carbocations are also carbocations they are also electrophilic in nature, but they are charged, ok. So, if they are charged obviously, when it will react; it will react with a nucleophile, ok. So, they are electrophilic, but charged and they will react with various type of nucleophile specially those type of nucleophiles which are having high charge density.

So, this carbocations reacts with nucleophiles, having high charge density, fine. So, this is the basic difference with the carbenes; carbenes are uncharged. Now, being such type of reactive species they will react with such type of compounds we would never consider them as nucleophiles. Like in case of carbocations, if they are having high charge density then only that will react with the carbocations, but in case of carbene it is too much electron deficient. So, it is very much hungry towards the electron.

So, what they will do they will react with various type of compounds which we even do not consider as normal nucleophile, ok. So, in case of carbenes react with compounds which we would never consider as nucleophiles. As per example lone pair carbon-carbon double bond, it could be electron rich or poor electron rich or poor even with carbon-hydrogen bond. So, various type of reactions it can give in general with different type of nucleophiles, ok.

Now, what type of reactions actually it can give? So, in general the carbenes and carbenoids we will consider both here. If we see their reactivities, so, first they will give we will or rather we will discuss about addition reactions. Number-2 is that insertion reaction, fine number 3 is that rearrangement reactions. Now, what type of addition reactions they can do? In principles they can be added to various type of unsaturated carbon-carbon bonds; so, can be added to unsaturated carbon-carbon bonds, ok. So, in general we will discuss these three type of reactions for the carbenes and carbenoids that is like addition reactions, insertion reactions and rearrangement reactions, fine.

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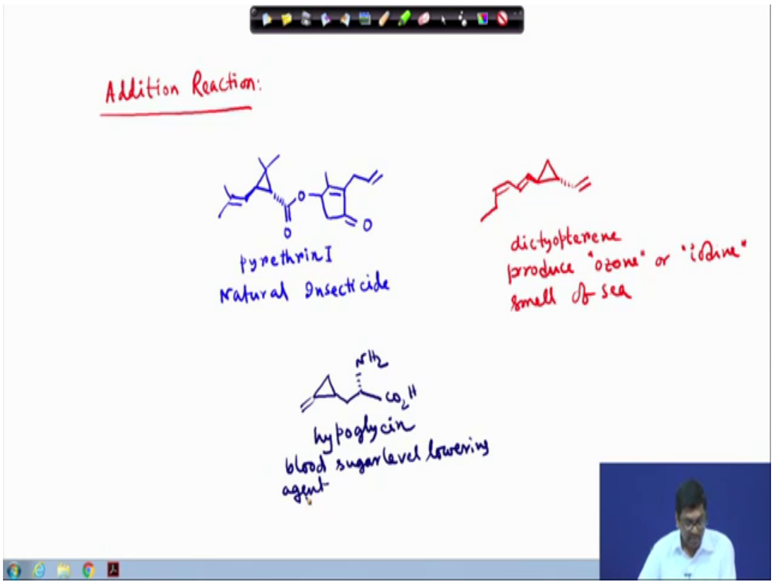

Next, we will start about addition reaction. So, what is this addition reactions? The name itself suggest that the carbenes will be added to something, ok, in general that is the different type of double bonds or triple bonds, fine. So, basically to the unsaturated carbon-carbon bonds there we can add these carbenes or carbenoids to generate various type of organic compounds that is called addition reactions. So, one of the easiest thing by these normal carbenes to make like cyclopropane. So, initially what we will learn we will learn that synthesis of various cyclopropanes.

But, why we have to learn this? Fine, what we have to learn the synthesis of various cyclopropanes. Let us see if we have seen the natural products chemistry or pharmaceutical type of chemistry then actually we can see that there are versatile cycloprapane compounds, cyclopropane ring containing compounds are available in the nature as well as in the pharmaceutical database that actually trigger to synthetic chemist to learn to synthesise various type of cyclopropane moieties.

As per example we can see that cyclopropanes like these. This is called pyrethrin I and this is a cyclopropane ring containing natural product and this is a natural insecticide, and this has been isolated from East African pyrethrum basis. Another cyclopropane ring containing by active product is this one. Dictyopterene, this also produces the smell like ozone or iodine in the sea. In the sea actually what about the smell of ozones or ozone type of molecules smell are coming that is actually not created by ozone or iodine.

Rather it actually a volatile cyclopropane compound and these has been used by female brown algae to attract the male gamets, ok. So, this is also this producing produce ozone or iodine smell, iodine smell of sea, ok. So, this is a bioactive compound and that actually produced by the female brown algae to attract the male gamets, fine. So, if you see these two compounds they all are having cyclopropane ring.

One more example we will learn. This is also another small example, the name of this cyclopropane containing molecule organic molecule name is hypoglycine. So, these what how it works this working to lower the level of blood sugar, ok. So, blood sugar level lowering agent and these has been isolated from unripe fruit of ackee tree, fine. So, these examples actually show that how cyclopropane ring is important because not only these three examples there are numerous number of examples are available where we can find that these bioactive organic molecules contain cyclopropane ring, fine.

Now, how we can synthesize this type of cyclopropane ring through carbine, ok.

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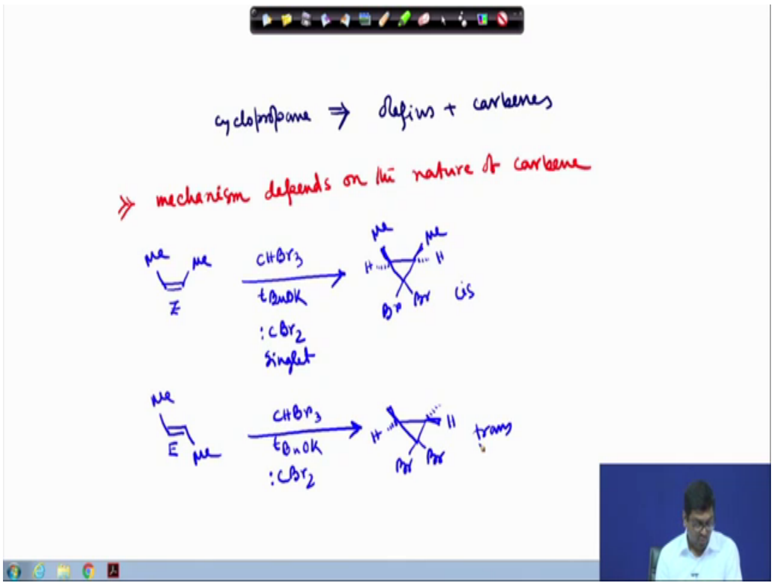
cyclopropane ⇒ olefins + carbenes

≫ mechanism depends on the nature of carbene

So, if we see it is retrosynthesis we can actually generate from olefins plus carbenes that can give the cyclopropane ring, ok. Now, what will be it is mechanism how will it work, fine. So, now, if we see this mechanism of reactions mechanism actually depends on the nature of carbene; that means, whether that is singlet or triplet. So, the mechanism of this reaction depends on the nature of carbine, ok. So, whether they are singlet or triplet depend upon that that it is reacts, ok.

In general these reactions outcome will chemically suggest that the reacting carbene is singlet or triplet. I mean that the carbene that we generated whether that is singlet or triplet. Obviously, spectroscopically we can measure them, ok. I have earlier also suggested the method that way you can actually identify whether the carbene is singlet or triplet, but chemically by this addition technique we can actually suggest whether these carbenes are singlet or triplet. Let us have a look that with the example, ok.

Let us take this Z olefin, ok. Now, if we react it with bromoform in presence of base that actually generate this carbene dibromo carbene that gives the cyclopropane ring, ok. So, here we know that this is a singlet carbene fine. Now, if we take this E olefin and under similar condition that means with this singlet carbene what we found the product is like this. So, in general this give this cis product whereas, this gives the trans product, fine. So, this shows that the additions of the singlet carbene towards the olefin will act via concerted manner, ok. So, how? So, the reactions of these olefins and the singlet carbene they will work in a concerted manner.

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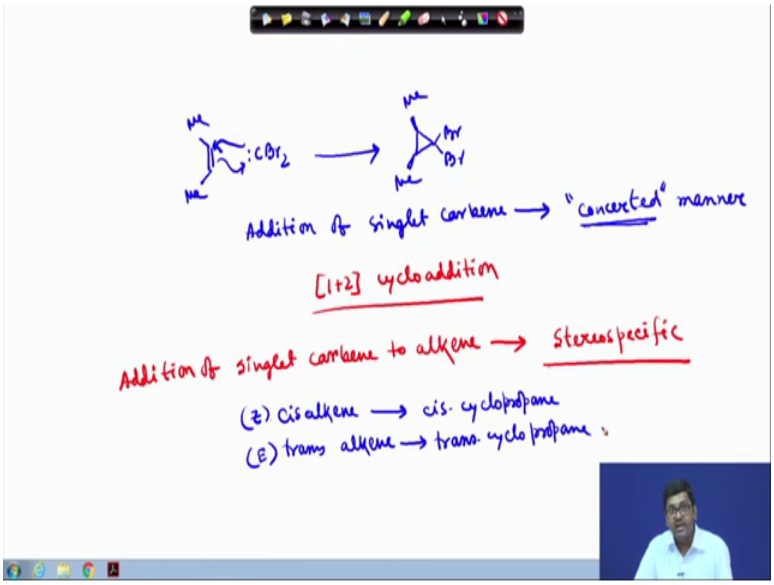

Addition of singlet carbene → "concerted" manner

[1+2] cycloaddition

Addition of singlet carbene to alkene → Stereospecific

(Z) cis alkene → cis. cyclopropane
(E) trans alkene → trans. cyclopropane.

Let us see how does it work, ok. Let us see you have this and CBr 2 now this can actually work in this concerted manner to give the corresponding cyclopropane. So what we can understand that the addition of singlet carbene actually happens via concerted manner, ok. So now, what is this concerted manner? That means, they are happening in simultaneous way; that means, it is not in step wise process that is happening in one step, ok, that is why we can call it concerted fashion, ok.

In general, these can be called as 1 plus 2 cyclo addition. Now, in this type of concerted reactions what happens the geometry of this starting material that is the alkene preserved in the product; that means, if we take here Z olefin here we are getting the cis product if we are taking the E olefin there we are getting the trans product, right. So, the geometry of the alkene is getting preserved in the product that is the cyclopropane stereochemistry that is why here these reactions are concerted.

So, next we can say that additions of singlet carbene towards the alkene is stereo specific reactions. So, addition of singlet carbene to alkene that is stereo specific, ok; that means, we are starting from one particular starting material and with a specific geometry or stereochemistry and in the product we are getting a specific stereochemistry, ok. So, if we are starting with Z olefin we are getting this cis cyclopropane and if we are starting with E olefin we are getting the trans cyclopropane these actually gives the idea about this stereo specific reactions, ok.

So, we can write from there that cis alkene that will give this cis cyclopropane whereas, this trans alkene here we can write Z and E; that means, Z means (Refer Time: 24:56) and E means (Refer Time: 24:58). So, this is giving the trans cyclopropane. So, it is obvious that when we are getting this type of reactions that is happening through the concerted manner via this singlet carbene then the reactions are highly stereo specific; that means, if we start with a particular stereochemistry of the starting material that will give the product with the particular stereochemistry.

So, overall these geometry of the starting material that is getting preserved in the product, fine and similarly if we start with a transalkene we are getting transcycloprapane. So, overall the geometry of these starting material, actually dictating that what will be the products stereochemistry, fine. So, in these way we can understand that these carbenes what we have used if they will give a stereo specific reactions then definitely the nature of this carbene is singlet.

Thank you.