Reactive Intermediates: Carbene and Nitrene

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Lecture - 02
Structure and Geometry of Carbenes

Hello everybody. So, welcome to my next lecture that is the Structure and Geometry of Carbenes ok.

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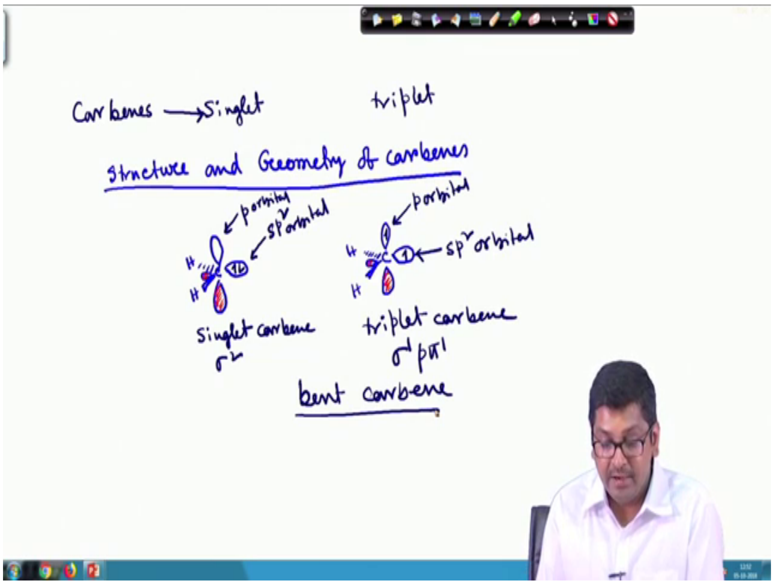

So, in the first class we have learnt about the introductions of the carbenes or rather reactive intermediates, where we have learnt that what is reactive intermediates, what are in general their characteristics and how carbenes as a reactive intermediate behaves and, what are their special characteristics among all reactive intermediates.

From there we have classified that carbenes are two types one is singlet, another one is triplet. So, singlet another one is triplet ok. So now, we will learn their structure and geometry. So, today in this lecture, we will learn structure and geometry of carbenes already, we have started that one these particular things little bit in the last course, we will continue that. So, in case of carbenes as we have already showed you still I would like to draw the same thing here for better understanding ok.

So, let us like different colour or here sorry so it will give ok. So, now we will fill up the orbitals ok. So, this is called singlet and here this is the sp 2 and this one is the p orbital similar here ok. So, this is called triplet carbene ok.

This is sigma 1 p pi 1 you can call it, because both these electrons they are occupying two different orbitals and here they are occupying in a single orbital ok, here they are paired up that is why there are called singlet. And, if you go through the multiplicity calculations actually that is why their name is singlet and triplet ok. So, in case of singlet this is the both of them has been paired up and in case of triplet, these are actually both are unpaired electrons and they are in two different orbitals. So, if we calculate the multiplicity, then as per that their name cames like singlet and triplet ok.

And it has in found their structures are bent. So, they are in general bent carbenes ok, theoretically or experimentally, it has been proved that they are bent in nature.

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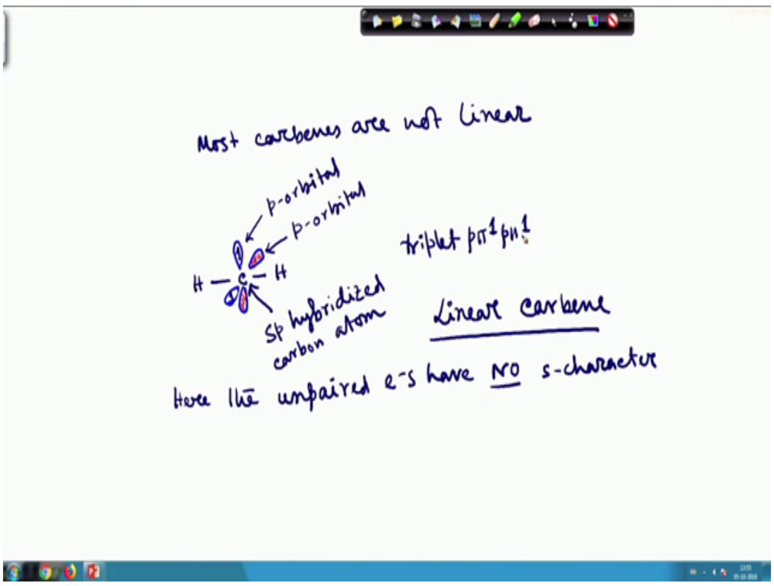

Now is there any linear carbenes, though they are rarely found or they are in general most carbenes are not linear, most carbenes are not linear, but still we can if it happens how it looks like ok. So, in this case we can actually put up these two electrons, we can draw in this way ok, this case we can draw they are orthogonally situated. So, ok so like this way so, here this is also p orbital this is the p orbital ok, these are the pure p orbital, this is also p orbital ok. And here this is linear and this is the sp hybridized carbon atom ok.

So, now these two electrons are totally occupying the pure p orbitals, they do not have any s character ok. So, these unpaired electrons here the unpaired electrons ok, have no s character so, this is called linear carbene ok. So, what we have learnt? That there are bent carbene as well as linear carbene even though, this is not very much existence this is not having so, much of existence, but still this is the linear carbenes structure and it looks like this.

And if you see this is also triplet and we can write it like this p pi 1 p pi 1 ok. So, what we have learnt that the electron electronic configurations of these carbenes are having like this, in some case if it is a bent carbene, they also have singlet as well as triplet and in case of linear carbine, they have this type of triplet carbenes ok.

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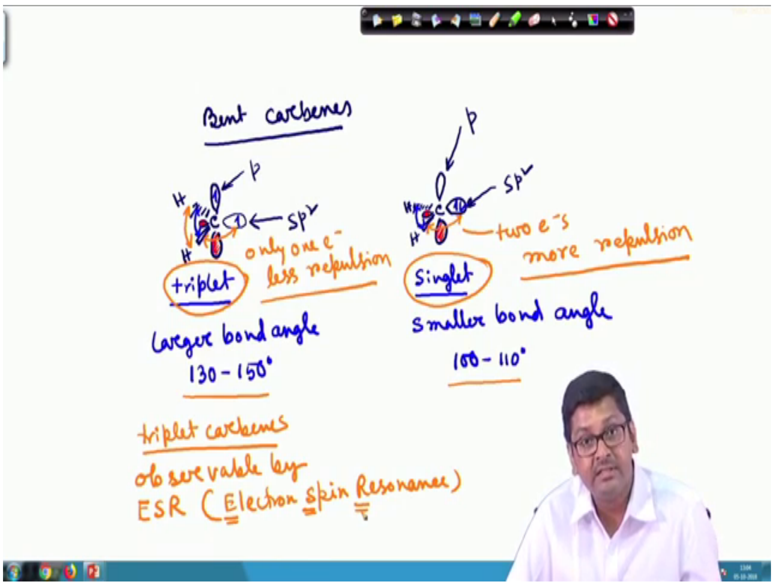

So, next if we see this bent triplet and singlet carbenes, this bent carbenes in general as I said the most of this carbenes are bent and that also experimentally and theoretically it has been proved.

So, what are their structures and how they are this bond angles behave see they are bent; that means, these particular carbenes. Let us say we can write like hydrogen here and this is having one sp 2 orbital 1 p orbital ok. So, next we can fill it up like this ok, now we can give the electrons so, this is for triplet so, this is for triplet carbene.

So, we have already drawn this, now we will draw again the singlet one ok. So, this is the two things. Now, for singlet carbenes it will be like this ok. Now, even though they are bent what will be there this bond angles; that means, we calculate this and this the bond angles, it has been found for triplet carbenes the bond angles are larger. So, this have larger bond angle and this is having smaller bond angle.

Larger bond angle means this is having around 130 to 150 degree and here it is having 100 to 110 degree ok. So, triplet carbenes are having larger bond angle. And the singlet carbenes are having smaller bond angle. Now, question is that why it is like this ok, why the bond angles varies for triplet and singlet.

Now, if we see that here for this particular singlet carbenes, they are in these sp 2 here it is sp 2 and the there this is this is the as you have seen sp 2 and this is the p here also same, this is sp 2 and this is p ok, we have seen this. So now, definitely these number of electrons are actually creating this difference. So, if you see here for singlet there are one pair of electrons ok, they have paired up.

Now, and in this case here there are only one electrons in this sp 2 and another one electron is in p. Now, if we see in this case the repulsion between these two here, only one electron ok. And here there are two electrons, definitely here it will be more repulsion than triplet case. So, for singlet case the repulsions will be higher than the triplet case.

And if this repulsion is higher then automatically here the bond angle will decrease ok. So, in case of singlet; that means, if it is two electrons, it is having more repulsion ok. And whereas, here it is only one electron so, this is having less repulsion and, if it is less repulsion; that means, this bond angle here this bond angles these will be larger that is here 130 to 150 degree and if it is the repulsion is higher, then this will have the smaller bond angle. So, this will have 100 to 110 degree.

One interesting point is here that triplet carbenes are actually experimentally you can prove, how there is one particular technique. If you do experiments always, we have to go through certain experimental procedures to identify, whether our products or intermediates that has formed or not right. So, we have done some reactions let us say as per example. And something we have reacted we got some products, but how we are identifying them ok, because after isolations of that particular reactions product we do not know whether they have formed or not. So, we have to take help of certain analytical techniques.

As per example NMR that is nuclear magnetic resonance spectroscopy or mass spectroscopy like, there are similar that kind of spectroscopic methods are available to determine the structure of the compound, here also for this particular triplet carbenes it can be observable by ESR ok. So, triplet carbenes so, triplet carbenes they are actually observable by ESR ok, electron spin resonance, spectroscopy so ESR.

So, this is called ESR spectroscopy or electron spin resonance spectroscopy, where if there is any unpaired electrons are available in the intermediate, you can actually identify them through this particular technique ok, but in case of singlet as it is paired up. So, it will not be visible, or it will not be characterized by this particular technique. So, in this way you can actually determine which one is triplet and which one is singlet by this spectroscopy ok.

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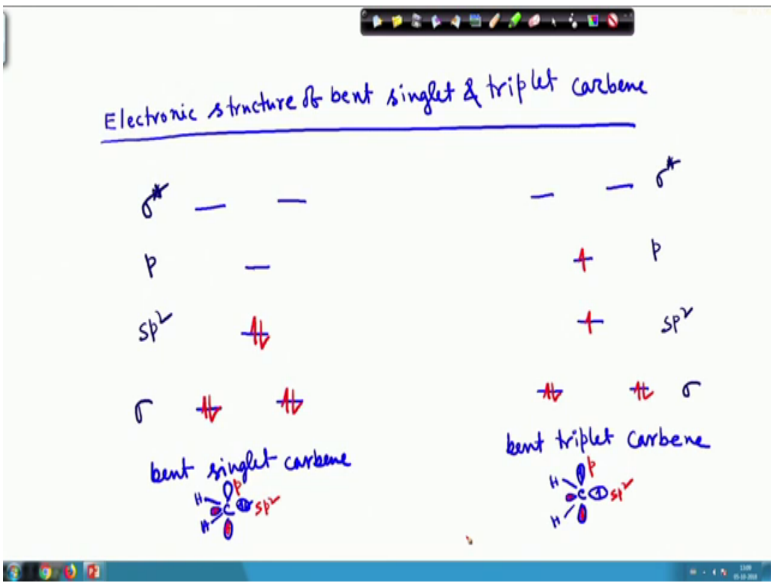

So, even though this bent carbenes are there like triplet or singlet, they have different bond angles we have learnt that why these bond angles are differ ok. So, it depends on their number of electrons, how they are actually occupying the corresponding orbitals ok.

Next we will learn the electronic structure of these bent singlet and triplet carbene. So, next what we will learn, we will learn the electronic structure of bent singlet and triplet carbene ok. So, first we will draw this bent singlet carbene that is I am just drawing like this way and so, if we draw their first they have this bonding orbitals ok. Next like this one and this non bonding so, we can write in general there these two sigma bonds, there this then one non bonding sp 2 orbital and 1 p orbital here ok.

mp p orbitals and in one case there is this anti bonding sigma star, we are stimulate here we have to draw like this ok. So, now, if we fill up the electrons as we know or we have already learnt that there are total six balancing electrons. So, we can fill up like this ok. So, this is the bent singlet carbenes that means, here this p orbital, this is the sp 2 here the p orbitals, we have already learnt this. Now if we see its molecular orbitals actually here it is like this. So, here this sp 2 orbitals that is actually having these two electrons and they are all paired up.

Similarly, if we now go for bent triplet carbene ok; so, like this so, here also this is sp 2, this is the p orbital unlike the singlet carbene here, both these orbitals are actually filled up with one electrons ok. So, now again we will do this similar way ok. So, now, again we can write like this sigma let us say this is sp 2 this is p this is sigma star so, if we start filling up this one electrons here these are the all these bonding's and then this sp 2 orbitals that is filled up with one electron and p orbital that is also filled up with one electron.

So, this is the bent triplet carbenes and there these orbitals are filled up in this way. So, these are their electronic structures and here actually these things guided that how they will behave ok. Next these are for the bent singlet and triplet carbene.

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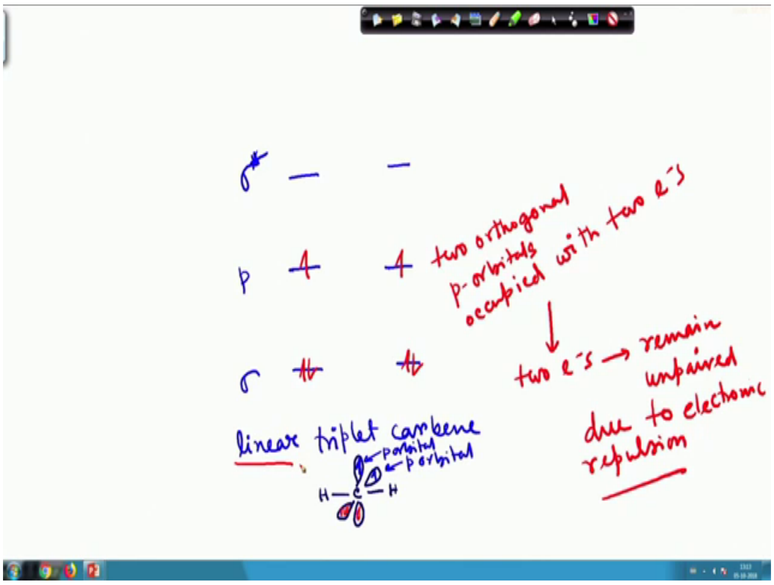

Now, if we see for linear triplet carbene how does it look like, so as per example like this so, this is the linear triplet carbene ok. So, it will be like this for example so C hydrogen and there will be two orthogonal p orbitals ok.

So this is the linear triplet carbene, this is the s p hybridize these are the p orbitals and this is the sp hybridized carbon atom ok. Now, if we again draw it is like that way here these 2 p orbitals, they are singular energy and then sigma star so two bonding, then 2 p orbitals ok. Now let us we filled it up so total 6 now they will stay like this, because these 2 p orbitals are same in energy ok and as they are same in energy so, these two electrons will occupy both of these 2 p orbitals ok.

So, here we can these are the two orthogonal p orbitals occupied with two electrons ok. And these two electrons these two electrons remain unpaired two electrons will remain unpaired, because of the electronic due to electronic repulsion ok. So, these kind of linear triplet carbenes rather as these two electrons they will remain unpaired. So, they can actually act like a diradical ok. So, what we have learnt? We have learnt the electronic structure of bent as well as linear triplet carbenes ok.

Thank you very much.