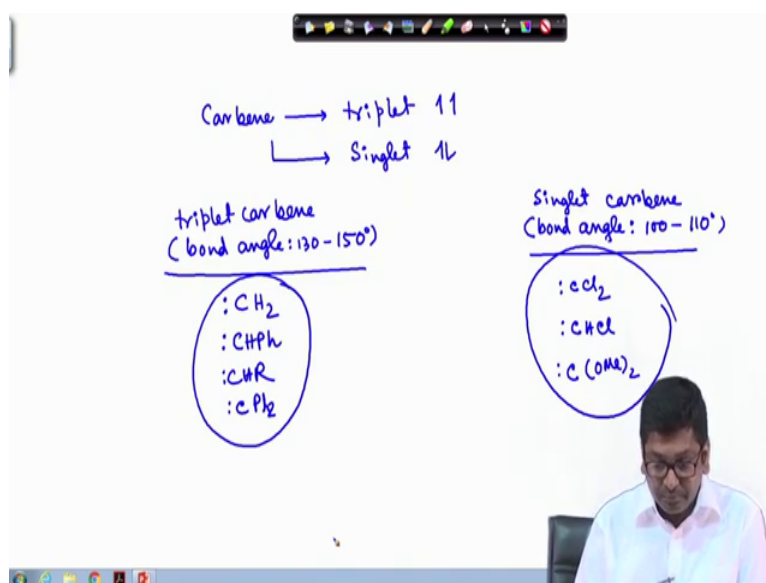


Reactive Intermediates: Carbene and Nitrene
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Lecture-03
Structure and Geometry of Carbenes (Contd.)

Hello everybody. So, welcome to my third lecture where we are continuing our topic that is on the Structure and Geometry of the Carbenes.

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So, today I will continue again on that particular topic; what we have learnt that carbenes are in general triplet and singlet right ok. So, once it is like this now the next questions will come into our mind that is which type of carbenes that will be triplet and which kind of carbenes that will be like a singlet.

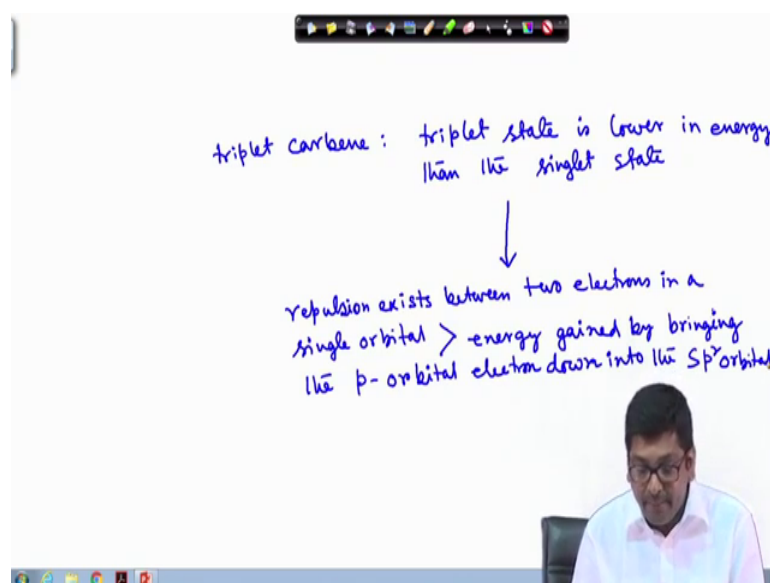
So, if we see in general triplet carbenes whose bond angles in general higher. We have discussed previously why its bond angles are higher; bond angle in general 130 to 150 degree whereas, singlet carbene that is its bond angle are in general 100 to 110 degree.

We have discussed its reason that why singlet carbene is less and why triplet carbene is more. However, here now you will see the examples in general the triplet carbenes that is like this. So, CH_2 and CH_2 carbenes; then $CHPh$ or CHR ; R here alkyl groups or

diphenyl carbenes and the singlet carbenes are dichloro or it is CHCl_3 or dimethoxy carbene ok; so, just examples few examples.

Now next question is that why these are triplet carbenes and why they are singlet carbenes ok. So, even though all these carbenes they can be stayed as triplet or singlet, but why some of these carbenes are actually preferring to be triplet and some of these carbenes are preferring to be singlet ok.

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So, now if we see something is triplet carbene means what? So, triplet carbene means triplet state is actually lower energy than the singlet state. So, it means triplet state is lower in energy than the singlet state. What does it mean? Again it means that if the repulsion exists between the 2 electrons in a single orbital is higher than the energy that gained by bringing the p orbital electron down to into the sp^2 orbital. So, basically if some carbenes is singlet means there will be 2 electrons in same orbital; so, there will be some repulsions.

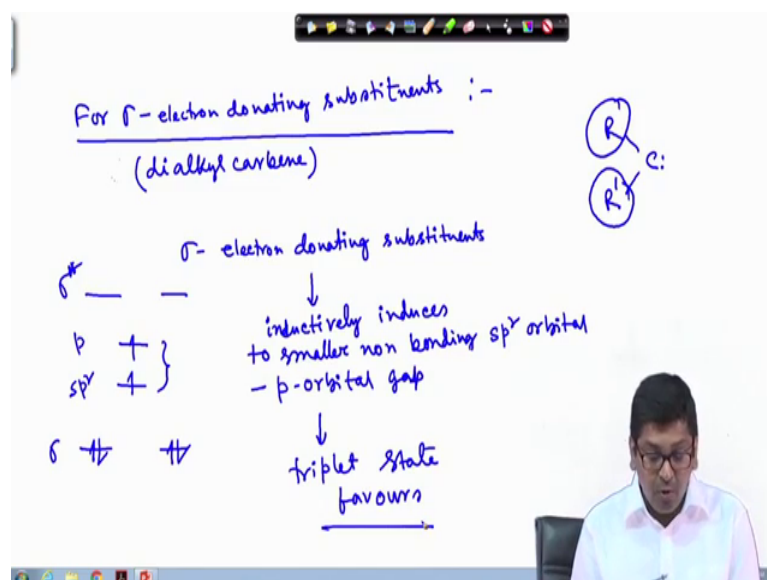
Now, if that energy is higher if that particular repulsion energy is higher; then we are getting or we are gaining the energy by bringing down the p orbitals electron into the sp^2 orbital; then basically that will be triplet ok; that means, the repulsion energy that is higher. Once it is like this; that means, always these carbene wanted to be triplet because in that case it will be lower in energy is it clear ok. So, we can write here that repulsion

exists between 2 electrons in a single orbital is actually greater than energy gained by bringing the p orbital electron down into the S p 2 orbital.

If we make it very simple that 2 electrons when it is in particular orbital let us say as for example, S p 2 orbitals; so they will have some repulsions; now that will have some repulsive energies. Now once something will be in a triplet state; so if we wanted to bring down that particular electron from p orbital to the S p 2 orbital; then it will gain some energy. Now depending upon which one is higher and which one is lower; now these carbenes will determine whether they will be in a triplet or singlet state ok.

Now if these gaining energy from bringing down from p orbital to S p 2 orbital; this gaining energy is higher than the repulsive energy then what it will be? Please tell if the repulses exist between the 2 electrons in a single orbital if that is the higher then; obviously, what it will be? Triplet, but if the opposite happens; that means, the energy gaining it is when you are bringing the electron from p orbital to S p 2 orbital that energy gaining is higher than the repulsive energy then; obviously, that will be singlet ok. So, now, we will see that what will happen when we will give let us say di alkyl; di alkyl carbenes ok.

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That means for sigma electron donating substituents, what will happen? For sigma electron donating substituents ok; so, what will happen for these things as per example di alkyl carbene ok. For sigma electron donating substituents that if that presents in the

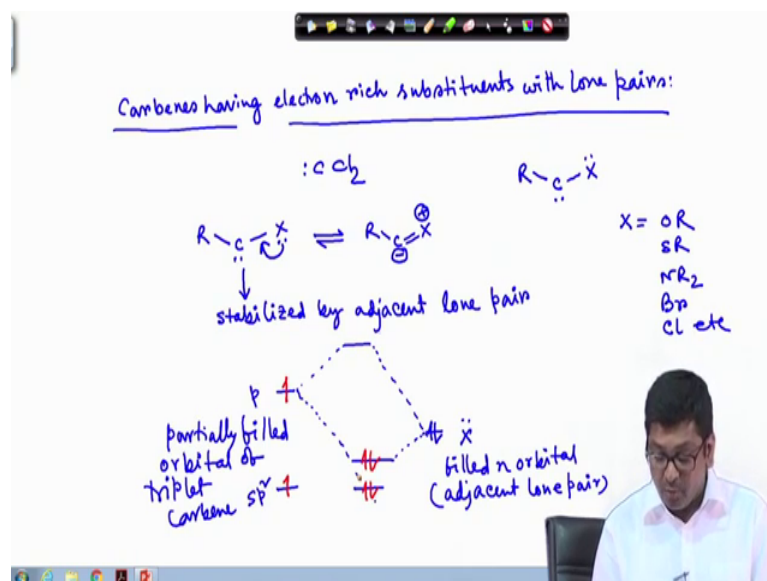
carbene; then how it will behave; once this sigma electron donating substituents is there what will it do? It will induce inductively; so, the.

So, what it will do? It will inductively induces to smaller non bonding S p 2 orbital and p orbital gap which favours the triplet state ok. If we see; if you remember in my last class I showed that how this can be shown in a electronic configurations; let us say like this. So, for this bonding we have given the sigma then this is like a S p 2 then p and then the sigma star.

Now we filled up these electrons like this for p orbital for this triplet. Now what sigma electron donating substituents will do? Now that is inductively induces to smaller nonbonding S p 2 orbital p orbital gap; ok. That means, to basically due to presence of the sigma electron donating substitution substituents in the carbenes; that means, like this; let us say like this. So, if these 2 are sigma electron donating substituents as per example alkyl groups, they will inductively induce to decrease the gap between the non bonding S p 2 orbital and p orbital. So, they will try to decrease this and once this energy will decrease then; obviously, these carbene wanted to stay as a triplet state because the energy difference between these S p 2 and p is now lower; so it will remain as triplet state. So, what will happen? Triplet state favors ok.

So, if you see in our previous slide there we have shown that as per example like this; here if you see I have shown that triplet carbenes; all are like this that parent our parent carbenes molecules CH₂ carbene CHPh or the alkyl group having alkyl group carbenes; those are actually stays as a triplet carbene.

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Next, we will see that carbenes having electron rich substituents with lone pairs.

So, previously what we have learnt? We have learnt carbenes having the substituents with the electron donating sigma electron donating substituents. Now what we will learn? We will learn carbenes having electron rich substituents with lone pairs ok; as for example you see this di chloro carbene. We can write this one like this now X arsenic lone pair this X could be OR, SR, NR₂; Br, CL etcetera um. So, now, we have all those things.

If this is the case then this carbene; this can be stabilized by the adjacent lone pair ok. So, these carbene can be stabilized by adjacent lone pair fine; how; how it can stabilize this one? If we see its orbital overlap ok; now this is the X that is having this lone pair; we can think like this and this is the S p 2 and p.

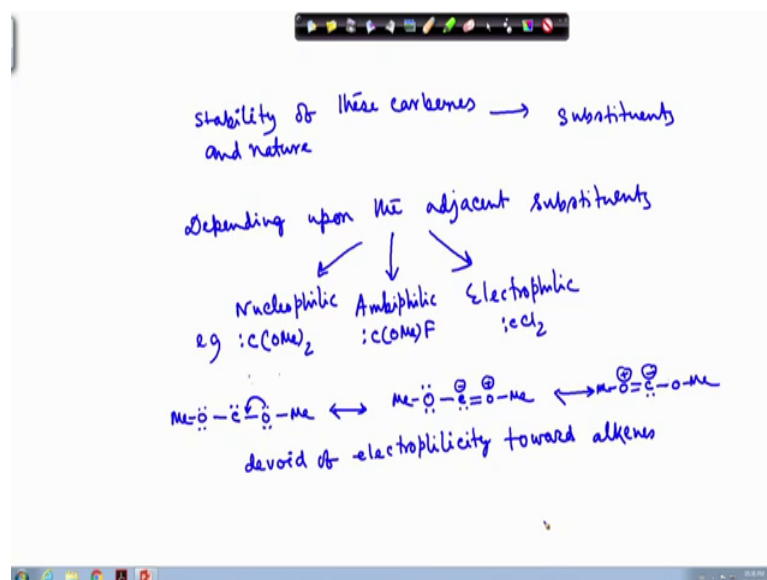
Now once these orbital will overlap they will generate lower energetic new orbitals ok; how it is now you will see. So, this is like this now this lone pair of this X, it can give to the vacant p orbital ok. So, now we will see that how these things can be filled up sorry.

This is we have done this one is pair ok; so now the electrons if you think. So, like this and like this and this is the filled n orbital, this is the adjacent lone pair. Now and this is a partially filled orbitals of triplet carbene, this is partially filled orbital of triplet carbene fine and this is the S p 2 nonbonding; this is the p. So, our p orbital and then finally, you

will get more lower energetic orbital, where it can stay as a singlet ok. So, what does it mean; that these adjacent lone pairs in these types of carbenes are actually stabilizing these carbenes as a singlet one clear?

So, the overall view of these particular type of carbenes is that when there is sigma electron donating substituents; then that is actually lowering the gap between the $S p^2$ and p . So, overall the energy difference is decreasing between them and as a whole it remains as a triplet. But the carbenes which are having electron rich substituents with lone pairs; they are staying as a singlet because of the filled n orbital of this adjacent lone pair that can stabilize, that can stabilize this type of carbenes and overall this type of carbenes are becoming like a singlets ok.

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So, now depending upon the adjacent substituents; how many type of carbenes can be, as you already mentioned that these stability of this carbene; stability of these carbenes are actually depending on their substituents or rather I should say not stability rather the nature of these stability and nature rather I will say stability and nature of these carbenes depending on the substituents right; the associated substituents with this.

Now depending upon that depending upon the adjacent substituents; depending upon the adjacent substituents there are 3 types of carbenes. One is called nucleophilic another one is ambiphilic and another one is electrophilic ok. So, there are 3 different types of

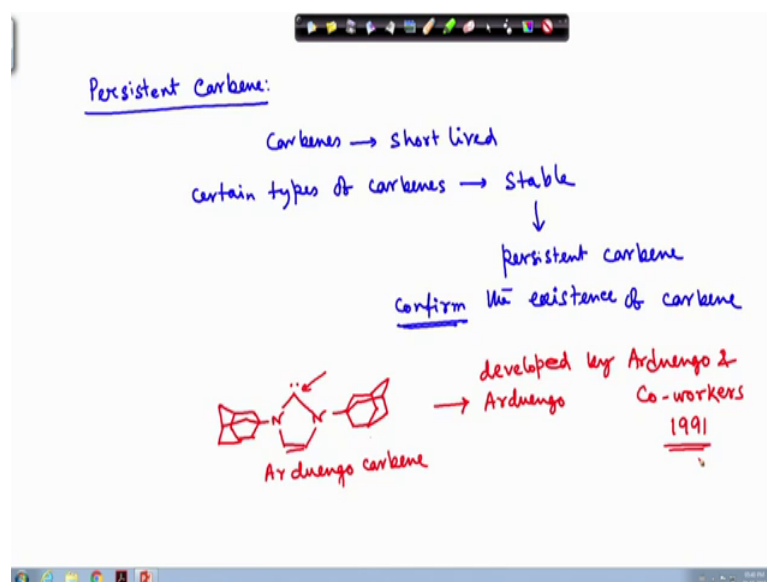
carbenes nucleophilic, ambiphilic and electrophilic; obviously, it depends on their adjacent substituents fine.

As per example nucleophilic is this I am giving one examples; this is example for ambiphilic, this is C OMe F carbene and for electrophilic; it will be dichloro carbene fine. Now if you see this particular type of carbenes, we have discussed this one this type of electrophilic carbenes. Now nucleophilic carbenes like this dimethoxy carbenes; they are devoid of electrophilicity towards alkenes why? Because of the electron donation by the methoxy group how?

So, if you see now that can give; so, in general it can be like this fine or it can be from this side. So sorry ok; so this type of carbenes that is why devoid of electrophilicity; devoid of electrophilicity toward alkenes because of electron donation by the methoxy group.

So, there are these 3 type of alkenes are there like nucleophilic, ambiphilic and electrophilic and in general these dimethoxy carbenes they are devoid of electrophilicity toward alkenes due to the donations of the electron by the methoxy group clear.

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Our next topic is that we will start that is called persistent carbene. What is this persistent carbene? In general we found that most of these carbenes; they are actually very short lived. Carbenes are in general are short lived ok; now there are certain carbenes which

are stable. Certain types of carbenes they are stable ok; these are called the persistent carbene ok. And; obviously, if some carbenes are stable and can be detected by various spectroscopic method then; obviously, this confirm; confirm the existence of carbene ok.

So, even though it is short lived, but due to presence of certain type of stable carbenes; we can confirm that carbenes are forming. As per example one of the very important example in this regard is this; this is called arduengo carbene ok. And in absence of oxygen and moisture; it exists as stable and colorless crystal whereas, its melting point is around 240 to 241 degree centigrade and bond angle is 102 degree of this carbenic carbon. In general in ^{13}C NMR spectra, it has been found that these carbenic carbon carbenic carbon that will give a peak at 211 PPM which reflects that this carbenic carbon is highly electron deficient.

And this particular carbene has been developed by Arduengo and co workers; developed by Arduengo and co workers and that is why these are called Arduengo carbene and this has been developed in 1991 ok. In the next class, we will learn why these type of carbenes are stable, what kind of factors made this stable and with that we will learn few more persistent carbene ok.

Thank you.