Reactive Intermediates: Carbene and Nitrene
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Lecture - 08
Reaction of Carbene (Contd.)

Hello everybody, welcome to my next lecture where we are going to study again the Reactions of Carbenes. We have started that addition reactions among there are three type of actually reactions we will study for carbenes, one is this addition reactions, insertion reaction and the rearrangement reaction. Now, we are actually studying the addition reactions. In the last class, we have already discussed about the addition reaction of alkene with a carbine.

And we have mentioned this addition is depending on the nature of the carbenes as per example if we take singlet carbine, it will give certain type of reactions; if it triplet carbine, it will give another type of reactions. There we have studied that singlet carbine, how they have reacted with the alkenes, and we found that the addition of this singlet carbenes work in a consorted manner, and they are reactions are highly stereo specific in nature.

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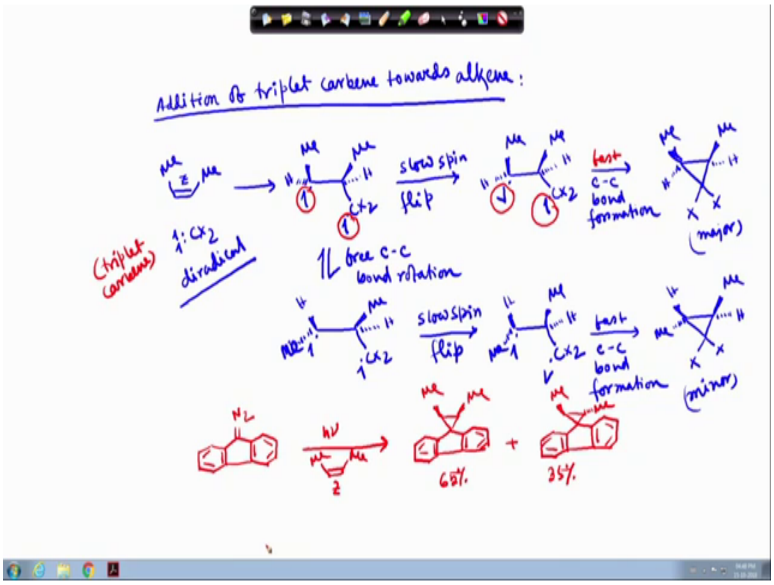

So, today we will learn the additions of triplet carbenes towards alkene. So, addition of triplet carbene towards alkene ok. So, how will they react? Like previous class again we can take this z olefine ok. Now, if we have this triplet carbene for better understanding I can draw in this way which we can actually this is the triplet carbene. So, in bracket we can write the triplet carbene ok.

And in general, we have previously mentioned that their behaviors are some kind of like diradical ok. So, now, this triplet carbine, how they will react with the olefin? So, if it reacts with this olefine initially it will generate this type of intermediate so something like this ok. Now, it can go for this slow step that is the slow spin flipping ok, otherwise it cannot make bond ok, both are having in similar type of spin. So, they cannot if you see they are similar type of spin, so they cannot make bond. So, thus spin flipping is required fine.

Now, once the slow spin flipping is happening, then it actually gives this electron that can give this spin flipping ok. So, now, they are having the opposite spin ok, they are having opposite spin, now they can make the carbon-carbon bond. So, this is the first step, and they can make carbon-carbon bond formation ok. Once they can make the carbon-carbon bond form or once they can generate that carbon-carbon bond, actually we will get our desired cyclopropane ring.

But here again we will get the cyclopropane ring with the similar stereo chemistry like the starting material. So, the overall geometry preserved here. But the interesting thing is that as this is going in this type of steps, so there is enough time opportunity that these particular intermediate that can go or proceed through this free carbon-carbon bond rotation, this is a single bond carbon-carbon bond. Now, it can rotate itself. So, free carbon-carbon bond rotations. So, once this will happen, then obviously the geometry will be scrambled as per example here it is like this ok, so something like this ok.

Once it will form this one, then again to prepare this cyclopropane ring, they have to make this carbon-carbon bond here, for that again this spin flipping is required ok. So, this spin flipping will work in this way ok, this spin flipping will work and giving the sorry here ok. If the spin flipping happens then obviously, this will work like let us say like this and then this two can make bond. And this first process that is the carbon-carbon bond formation that will give our desired cyclopropane ring, but with a different stereochemistry ok.

So, if you see here that incase of singlet carbene only single product form ok, so preserving the stereochemistry, but in this case there is a scrambling of the stereochemistry. Here I would like to mention that this spin flipping that generally occurs through the collisions with another molecule in general in the reactions there will be solvent. So, with the solvent molecule if it collides then only, it can go for the spin flipping ok. So, once this spin flipping happens then only, it can make this carbon-carbon bond ok.

So, addition of this triplet carbene towards alkene, we can call these reactions as stereoselective ok. So, here streochemistry of this starting material has been scrambled, and the rotation in the intermediate through this carbon-carbon bond triggers this kind of scrambling of the stereochemistry. Here and that gives this two different products, here it is happening this one is major product in the reactions and here it is the minor product in the reactions, but here; obviously, we are getting the mixture of two product ok. Even though we are starting from one particular stereochemistry that means, we are taking one olefin z olefin, but we are ending up getting two different cyclopropane product that is one is cis another one is trans fine.

As per example we can see if we photo chemically irradiate this diazo compounds, then that can generate the carbenes. And what we found in the product that this is z in the product, it generates that cyclopropane like this plus ok. So, this is around 65 percent and this is around 35 percent. So, from this outcome of this reactions, we can suggest that definitely the carbene that generated by this photochemically radiation of this diazo compounds is actually generating triplet carbene ok. So, what we have initially suggested that these chemically we can prove that the nature of this carbene through this addition reactions ok.

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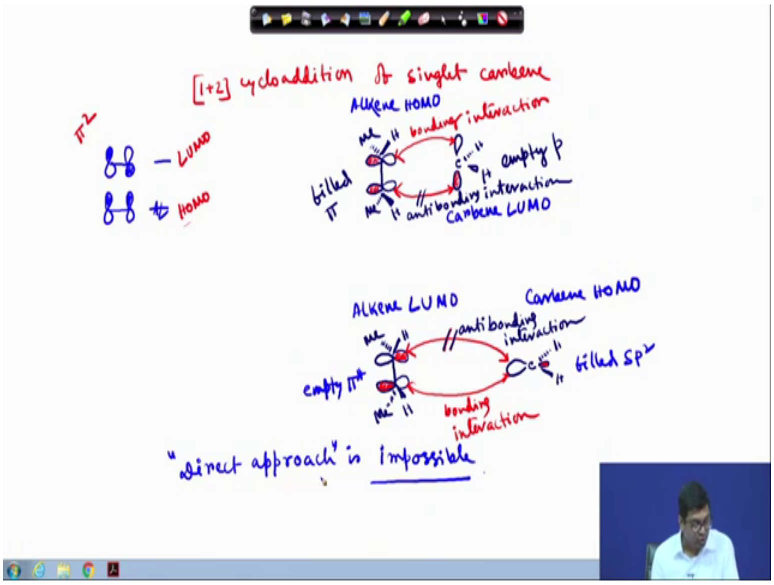

Next, we will see during the addition of these concerted reactions via the singlet carbene through orbital symmetry approach ok. So, let us see how does it work these 1 plus 2 cyclo addition reactions of this of singlet carbene ok. So, before that we know that the in general the alkenes we draw its orbitals, we see that so here this is the HOMO and this is the LUMO ok. So, LUMO means lowest unoccupied molecular orbital and HOMO means highest occupied molecular orbital ok.

So, for these pi 2 system, so this is the pi 2 system, this should be it is orbital molecular orbitals ok. Now, if we take alkene HOMO, because we are reacting with a olefin having pi 2 electronic system with a carbene fine. So, let us draw its orbital, let us check its orbital symmetry. So, we have taken this z olefin and so this is the alkene HOMO so this is alkene HOMO ok.

Now, we will see the carbenes LUMO, because the alkene HOMO will react with the carbene LUMO. So, if you see the carbene LUMO, so this is the carbene LUMO, where this empty p orbital is there. So, this is the empty p orbital, and this is the filled pi orbital. So, in this case, the empty p orbital that is the carbene LUMO. So, this is the, we can draw like here. So, this is carbene LUMO. So, alkenes highest occupied molecular orbital is this we have drawn over here like this way, and this is the carbenes lowest unoccupied molecular orbital ok.

So, now if we see that how they can generate this bonding let us say if we check it is nicely making bonding interaction ok, but you want to make like this definitely this is not giving the bonding interactions rather, this is giving the anti-bonding interactions. So, this is the bonding interaction, and this is the anti-bonding interaction ok. So, in this way definitely through this direct approach of in this direct approach, we cannot make complete bonding. So, definitely this type of approach is not happening. Now, if we take in opposite way, here we have taken alkene HOMO and carbene LUMO.

Let us take the opposite one that means, we will take the alkene LUMO and carbene HOMO. So, let us draw this alkene LUMO here already we have drawn that ok. Now, filled up so here, we can like this so this is the alkene LUMO now we will draw the carbene HOMO ok. Now, let us check how this, this is the, this is the filled S P 2, and this is the empty pi star orbital ok. So, here this filled 2 filled S P 2 orbital that is acting for the carbene as highest occupied molecular orbital. And in case of alkene the lowest unoccupied molecular orbital is this empty pi star fine.

Let us check whether their bonding is if you see this one, this is nicely giving the bonding interaction ok, but this one is anti-bonding interaction ok, so this is the anti-bonding interaction fine. So, in this case also if we see that these two direct approach are not possible for these type of cyclo additions with singlet carbene. So, here we can mention that direct approach for this singlet carbene is impossible, because if we see that this is giving some anti-bonding interaction through this direct approach ok. So, this is not possible, but the reactions are happening. So, how this reactions are actually working that we will see now ok.

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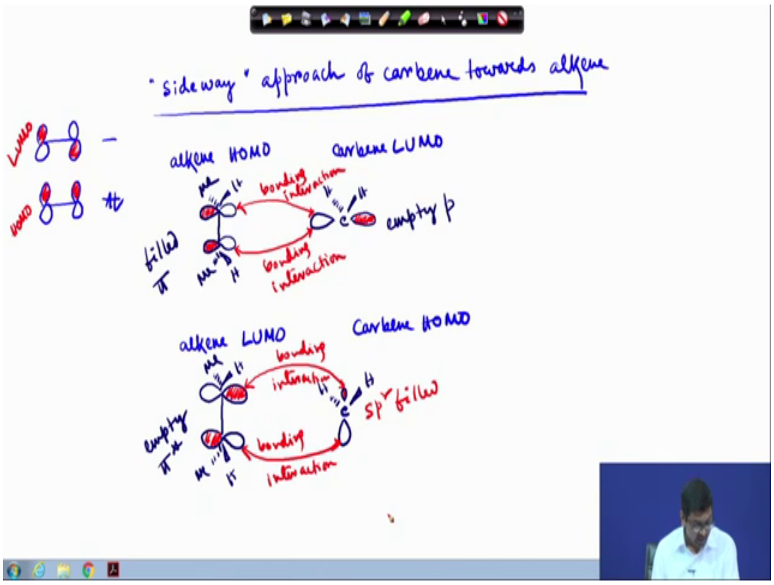

So, let us have a look the sideway approach of carbene towards alkene. So, now, we will learn the sideway approach of carbene towards alkene. So, direct approach does not work for this addition of this carbene towards the olefin ok. So, orbital symmetry is not approving that. So, let us see that how the sideway approach is working. So, here if we see again, we will take the alkene HOMO and carbene LUMO. So, we will draw that again ok. So, we have taken this z olefin ok. Now, it is HOMO means. So, this is the corresponding olefins highest occupied molecular orbital.

Now, you will see it is LUMO that means, the empty p orbital that we will see we have seen when it is directly approaching in my previous slide or previous slide, we have seen that when it is directly approaching, this is not giving the bonding interactions, so that becomes impossible. Now, we will see the side approach of this particular empty p orbital. So, here it is ok. So, this is the p orbital of this carbene. So, this is the empty p orbital, and this is the filled pi orbital fine.

Now, if we see that the side way approach, it is nicely giving this bonding interaction ok. So, both way it is giving the corresponding bonding interaction. Here also bonding interaction; here also bonding interaction fine. So, in these way actually the alkene HOMO and the carbene LUMO if the sideway approach can be considered, then definitely this orbital symmetry is happening ok. And in this way these reactions can nicely takes place.

Now, we will check in opposite direction, we have checked previously also in two different way that taking alkene HOMO and carbene LUMO as well as carbene HOMO and alkene LUMO, but that does not work ok, because these are giving the anti-bonding interaction. But here in the sideway approach of these carbene towards alkene, what we found these alkene HOMO is nicely making this bonding interactions with the carbene LUMO. Let us see the opposite way that means now we will take the alkene LUMO and carbene HOMO that means, now we will take the alkene LUMO that means lowest unoccupied molecular orbital you see. So, like this pi 2 electron system so and filled up like this, something like this ok. So, here this will be HOMO, and this will be LUMO, we have shown previously also.

So, in this case, this is the alkene LUMO we will draw ok. We will take the corresponding alkene LUMO that is this. So, this is the LUMO means this is the empty pi star, and we will take the corresponding carbene HOMO that is this one, so the filled up sorry. Now, we will check it is interaction here also bonding interaction and here also bonding interactions ok. So, this is the bonding interaction and here also the bonding interaction.

So, both the cases so here we have taken the s p 2 filled orbital, and this is the empty pi star orbital, and this has been considered as alkene LUMO and this s p 2 filled that is the carbene HOMO. So, in this case both the sideway approach are actually giving, the interpretations that how these carbenes are actually reacting with the alkenes ok.

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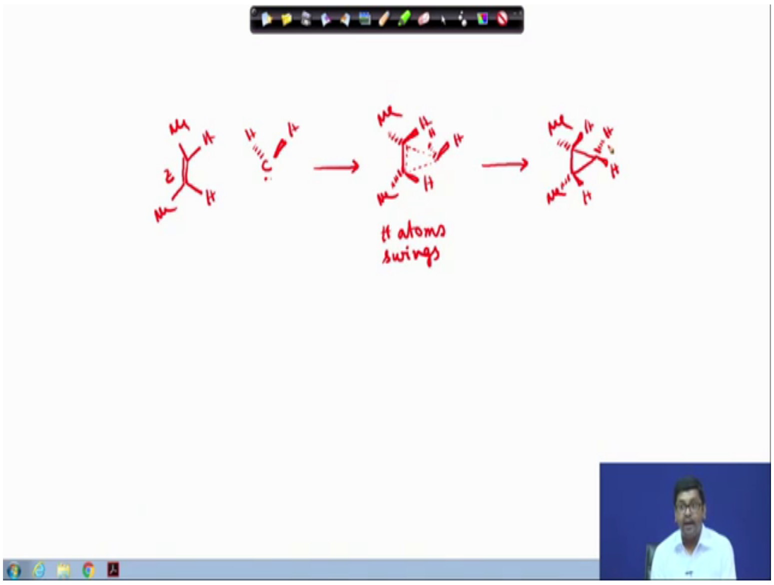

If we see these cyclopropane product, they are almost tertrahedral arrangements they are having. And if you see that they are reacting reactions, they are actually starting from like this say it is z. So, if you see these carbenes ok, so in general how they are reacting ok. So, so the hydrogen atom swings round into place, so hydrogen atoms that swings to give this tetrahedral type of arrangement. And finally, that gives the cyclopropane ring with this stereochemistry ok.

So, this is the overall approaches that direct approach, sideway approach that shows that where this bonding interactions are happening, where not. And this way we can actually interpret that how these 1 plus 2 cyclo additions for this singlet carbenes happening in this concerted manner and how they are stereo specific reactions happening with this type of singlet carbenes.

Thank you very much.