Reactive Intermediates: Carbene and Nitrene

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Lecture – 16
Nitrene

Hello everybody. Welcome to the course Reactive Intermediates, Carbenes and Nitrenes. So, today we are going to discuss a very important part of this topic that is called Nitrene. This is also this nitrene also similar to the carbene very much reactive, and they are short lived. And in general all the different aspects of this nitrenes are almost similar like a carbene ok.

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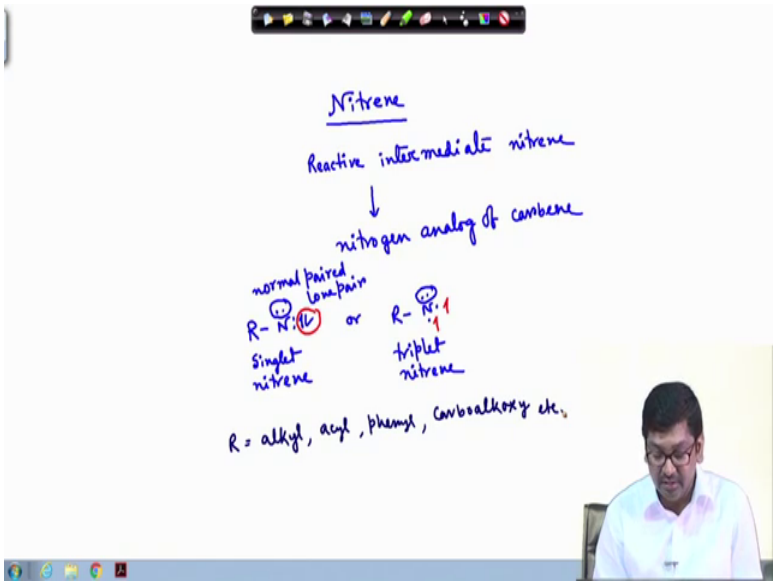

So, today what we start then that is called nitrene. So, these reactive intermediate are actually nitrogen anolog of carbene. So, this one is the nitrogen analog of carbene ok. So, we know that carbenes are short lived species, and they are very much reactive. Similarly, this nitrenes are also very much short lived in general, and they are also very much reactive species.

Now, if we see their netronic structure so in general, they could be this or they could be like this, now this is called singlet nitrene, and this is called triplet nitrene. If you see that nitrogen is having their own lone pair that is this one, that is the normal paired lone pair this is the normal paired lone pair ok, here also the same thing.

Whereas, there are these two electrons are there that either could be paired off or they can stay like this as a triplet nitrene ok. So, in general what are these R? This R are could be alkyl ok, acyl, phenyl, carboalkoxy etcetera ok. So, if we see that this species this reactive intermediate species that is nitrene, they are like a singlet or a triplet, and they are nitrogen analog of the carbene, where their R could be alkyl, acyl, phenyl etcetera ok.

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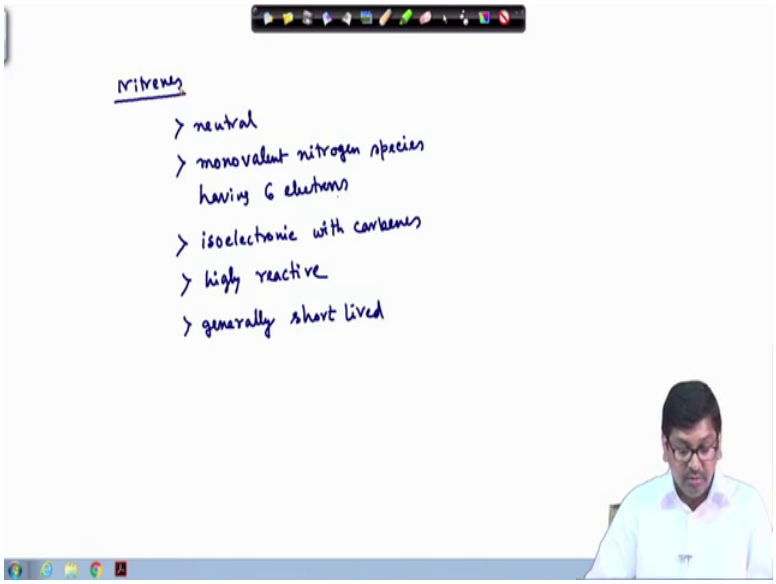

So, what are their characteristics? As I mentioned previously that they are the nitrogen analog we can say of carbenes. So, they are neutral species, and obviously they are monovalent nitrogen species having 6 electrons ok. And, they are isoelectronic with carbenes, because in case of carbenes also we found, there are they are highly electron deficient species, they are having only 6 electrons.

Similarly, nitrenes are also same. They are also isoelectronic with carbenes, they having these 6 electrons with them. And obviously, they are highly reactive species ok. Generally short lived ok and with these all these characteristics for these nitrenes are actually matching with carbenes, but still there are certain aspects or certain reactivities that is differing different than the carbenes. Why it is like this, we will discuss that also ok.

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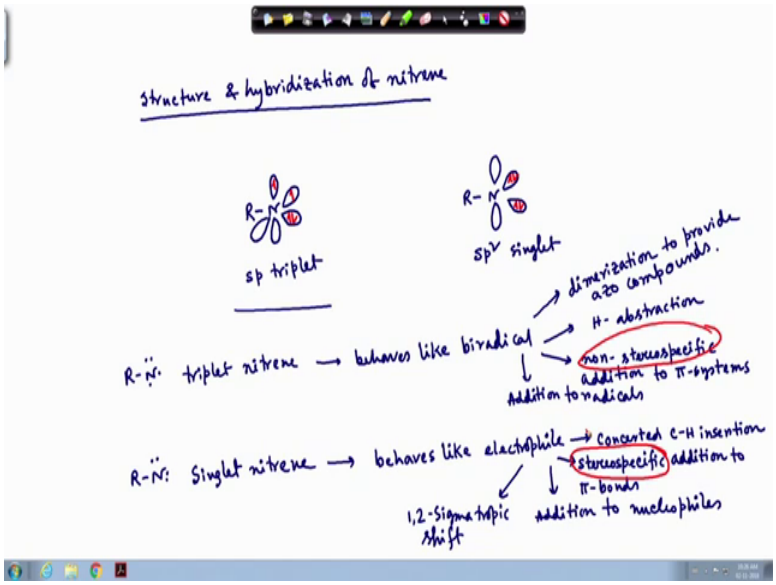

So, now we will see the structure and hybridization of nitrene, so structure and hybridization of nitrene ok. We have seen in case of carbene, how they are like a triplet and singlet what are their hybridizations, how they are staying like sp two singlet or triplet, and what are their how what will their bond angles, those things we have discussed. Here for this particular nitrene species as they have also 6 electrons with them.

So, in general this nitrenes they are having these either triplet s p or singlet, s p 2 type ok. So, now we have total 6 electrons with them. So, now one is this bonding one pair of electrons. Now, another two electrons that is these are the nitrogens that lone pair that could be there. And that two electron two valence electrons, they will stay almost nearly degenerate non-bonding molecular orbitals, they will stay in their parallel spin.

So, these two valence electrons, they wanted to stay in these non-bonding molecular orbitals in parallel spin ok. So, these two electrons they will stay in this non-bonding molecular orbital ok. What about this one, this is s p triplet ok, where s p hybridizations and this is a triplet, because both are unpaired electrons, and they are with the parallel spin.

Now, another possibility that nitrenes are generally staying as a s p 2 singlet, this non-bonding molecular orbital. And here they can be the 6 total electrons. So, one is two are

here as a bonding electrons, then these two are lone paired electrons, they are also paired up. And another two electrons, they can be paired up and space here, so that they are will be in a singlet state. So, this one we can say that s p 2 hybridized, nitrene this center is s p 2 hybridized, and then s p 2 singlet ok.

So, in these case this two nitrenes, one is s p hybridized, another one is s p 2 hybridized. And in this case to un pair electrons are there in parallel spin, they are that is why s p triplet. And in this case this electrons to electrons unpaired electrons we can paired up, and they stays like a this nitrogen here. This center is s p 2 hybridized, and that is in a singlet state ok.

In general, it has been found that nitrenes are generally linear, and it has been found that triplet state that is this one. Triplet state is lower in energy than singlet state ok. So, in the ground state this is their triplet state that is lower in energy than the singlet state ok. Now, once this type of nitrene formed like triplet nitrene or singlet nitrene, in case of triplet nitrene, which actually behaves like a biradical behaves like biradical ok. We have seen in case of carbene also, where it is triplet carbene that time also we have mentioned that in that case the triplet carbene that also act like a what biradical.

Here also this triplet nitrene, they can behaves like a biradical. And as that is unpaired electrons are there, so in that case obviously spectroscopically these can be again understood or these can be again these can be experimentally, these can be examined whether this triplet nitrene as formed or not through spectroscopy also we can measure for this triplet nitrene ok.

Now, what they will do as a biradical, what type of reactions they can do, this can actually do hydrogen abstraction reaction or similar like a carbene, we have seen that in case of carbene also when it is triplet carbene, we have mentioned that when it is adding to any pi systems most like the double bond or olefins that is giving the non-stereo specific additions that means, after additions of this triplet triplet carbene, what happens there is it is not stereo specific anymore that means, we are getting mixture of products.

In these case also when we have used the triplet nitrene, they also behaves in similar mode of fashion that is they will also give non-stereo specific addition to pi systems or else as it is also like a behaving like a biradical that can also added to another radicals.

So, addition to radicals or these two nitrenes, they can dimerize their selves. So, another reactions cam be possible from this triplet nitrenes that is the dimerization of the nitrenes to provide the azo compounds ok. So, these different types of reactions can be possible with the triplet nitrene ok. And we have seen that this is also working in a similar fashion like carbene ok.

Now, singlet nitrene what will be their reactions what kind of reactions, they are proceeding. So, if we take singlet nitrene we can write here or here we can write sorry some mistakes ok, now the singlet carbene like singlet carbene, singlet nitrene also behave in similar way. One important aspects for this singlet nitrene is that it is having one empty non-bonding molecular orbitals ok. This haves what one empty non-bonding molecular orbital. And that has capability to accept electrons from other sources.

So, in that case these type of singlet nitrenes, they actually behaves like electrophile so behaves like electrophile ok. We have seen even though they are analogous to carbene, but due to their structural features that nitrenes are actually giving different type of some different type of reactions, then the carbenes because of their structural aspects ok.

So, in that case if this singlet nitrene is behaving like a electrophile, so what type of reactions they can give that in general the singlet nitrenes that obviously, this is a s p 2 singlet nitrenes, and then they will give similar like a carbene type of addition reactions, and that is obviously in a concerted manner. So, whether this is insertion into carbon hydrogen bond or whether that is insertion into sorry not addition into some pi bonds all will be stereo specific.

So, we can think about that this will give concerted carbon hydrogen insertion ok. Next it can give stereo specific addition to pi bonds or as this is like a working like a electrophile that means, this is having some empty non-bonding orbital. So, in that case the nucleophiles can also attack to the nitrenes. So, we can write that addition to nucleophiles or they are could be similar like a carbenes, here also it is possible shift that 1, 2 sigma tropic shift.

And obviously, this type of sigma tropic shifting will lead to different type of rearrangement reactions, which we will discuss during our reactions and rearrangement part of this nitrene ok. So, overall what we have seen that even though this nitrenes are

the nitrogen the analog of the carbene, they are the isoelectronic, but with the carbene but still due to their structural features, they will have certain different type of reactions or reactivity in one case triplet nitrene that is the in general that is s p triplet nitrenes. They behaves like a biradical and gives different types of reactions like dimerization, hydrogen abstraction, non-stereo specific addition, and additions to radicals.

This is important that here this triplets will give this non-stereo specific additions ok, whereas this stereo specific additions. This is a similar like a carbene. Additionally what we said that this triplet nitrenes, they can be understood through some ESR spectroscopic ok.

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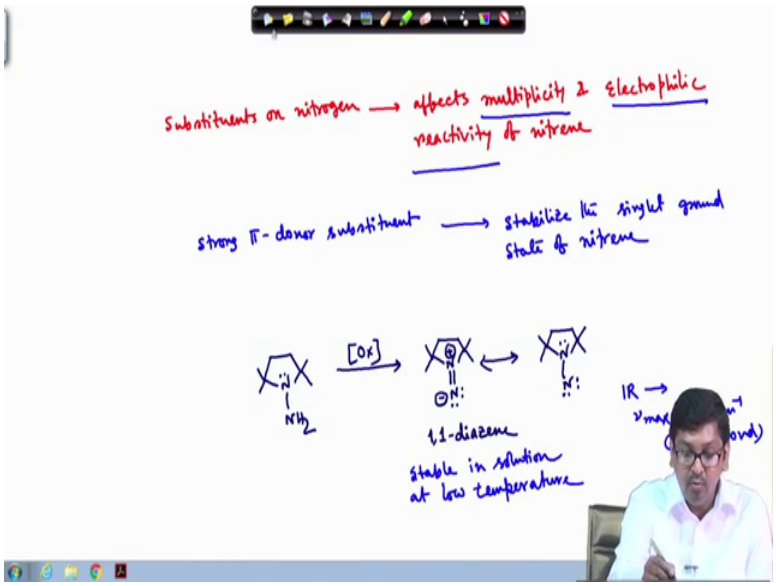

Now, next what we will see that how these nitrenes stability differ with the substitution on the nitrogen ok. So, if you put substitution on nitrogen, that actually an on specific type of substituents that actually stabilize these nitrenes, and it is possible to detect these even though they are very much shortlived (Refer Time: 19:56) species. But, reactive species, but this could be actually under so this could be actually stable in solution at low temperature ok. So, it can be detected to various spectroscopic technique as per the infrared spectroscopy ok.

So, if we now substitute put this substituents on the nitrogen, that what will change that affects the multiplicity ok, and obviously electrophilic reactivity of electrophilic

reactivity of nitrene ok. So, in general that affects the multiplicity and the electrophilic reactivity ok. If we (Refer Time: 20:55) as per for example, if we take strong pi-donor substituent, which could stabilize the singlet ground state singlet ground state of this nitrene. So, if you take this strong pi-donor substituent ok, then what that will that will stabilize the singlet ground state nitrene ok.

So, we will take one example like if we use one amino 2 2 pi pi tetra methyl pyrrolidine that is this molecule, this is a pyrrolidine moiety, and this is two two pi pi tetra methyl pyrrolidine. And if you take it is 1 amino 2 2 pi pi tetra methyl pyrrolidine this substrate, then under oxidation condition what will happen, if you oxide this, so basically that will generate the nitrene and ok, it will be stabilized, and this is a singlet state that generates ok.

And this is actually in resonance. So, initially this nitrene will generate ok, and these could be in resonance with these species that is this is called 1 1-diazene ok. So, this is the 11-diazene that will be formed, and it is stable in solution at low temperature. So, this is stable in solution ok. So, what happens, we took this 1 amino 2 2 pi pi tetra methyl pyrrolidine, this is called one amino 2 2 pi pi tetra methyl pyrrolidine.

And if we take this and oxidize this that will form, this 1 1-diazene species, and this is the nitrene species that could be stable in solutions at low temperature, because of this these this is having this nitrogen among this nitrogen here this is the substituent that is actually stabilizing this unstable reactive intermediate nitrene here ok.

And in principle these species actually could be visualized through IR spectroscopic. One spectroscopy is there through that we can actually visualize different type of whether that some organic molecules are formed or not or some due to some stretching frequency of that particular typical particular bond, we can understand that whether that functional group is present or not through these particular spectroscopy. So, this is called IR spectroscopy. And in these in through these we can actually here nu max is around 38 eight centimeter inverse ok, so due to this bond ok. So, through IR it can visualized, and it can be detected.

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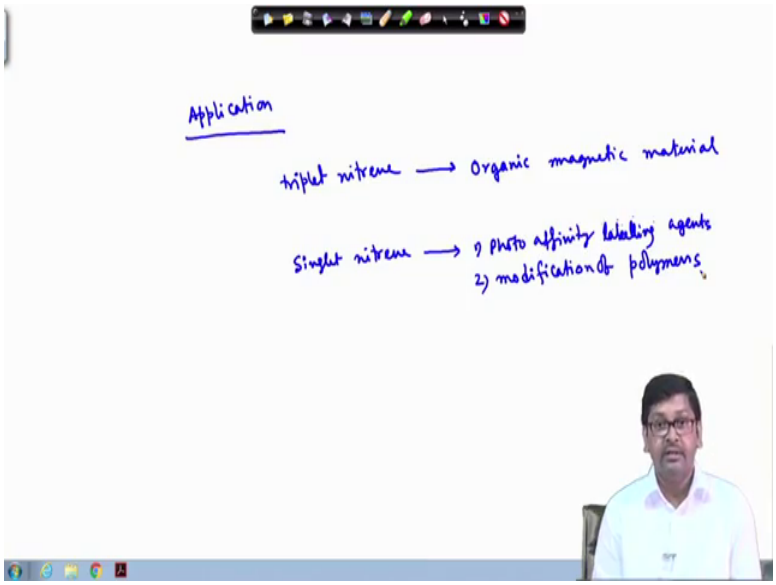

Now, what are the application? So, of course that nitrenes are generating and what will their applications in various type of reactions. So, if we see their applications, in case of triplet nitrene, as they are having these unpaired electrons and they are behaving like a biradical, they could be a very good species for as a organic magnetic material. So, they can be used as organic magnetic material ok. And there are enormous research is going on this particular field where triplet nitrenes are actually used as a organic magnetic material. And this is very important aspects or very important applications in terms of triplet nitrenes.

Similarly, for singlet nitrenes as this can be used as a electrophile, so this is having one empty non bonding orbital. So, it can accept electrons from other very easily; many industrial and biological applications where their due to their ability to insert into a surroundings chemical bond. So, if there is any chemical bond which are having this electrons, so this is a electron deficient species this wanted to take electrons. So, definitely what will happen this can be inserted into that particular chemical bonds depending upon the situation and that is why this can be used as a photo affinity labeling agent.

Because once you can insert this ok, if this lets say this singlet nitrene contains some fluorescent part ok, and then if this after generating the nitrene, if it can be inserted into proteins, then basically we can visualize that particular protein as these nitrene that is

having these fluorescent part that is there. So, we can actually now visualize these proteins ok, and proteins through various provision spectroscopy and that way we can use this singlet nitrenes for the photo affinity labeling agents ok, sorry photo affinity labeling agents ok.

And number two they can be used as to modify different type of polymers, so modification of polymers ok. So, this different type of reactions or different type of applications is there for triplet nitrene as well as for the singlet nitrene ok. So, we have discussed various applications of triplet and singlet nitrene.

Thank you.