Reactive Intermediates: Carbene and Nitrene

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Lecture – 18
Reaction of Nitrene

Hello everybody, welcome to my course that Reactive Intermediates Carbines and Nitrenes. We have already studied all about carbines and we have started about nitrenes. For nitrene already, we have discussed about it is electronic configuration, hybridizations etcetera.

So, today we will discuss about varieties of reactions that we associated with nitrenes as per example ok, so, reactions of nitrenes.

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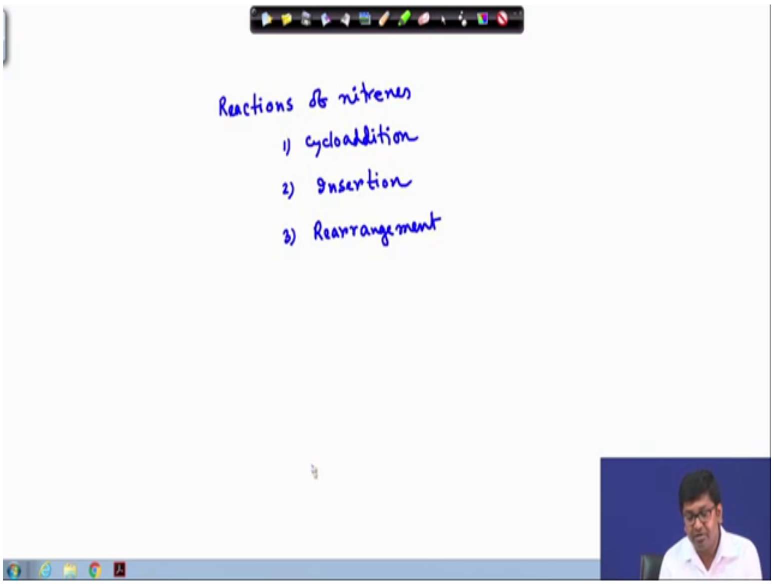

Reactions of nitrenes
1) cycloaddition
2) Insertion
3) Rearrangement

So, basically we will discuss the cyclo addition of nitrenes, similar like carbines. And in case of cyclo additions, we will discuss the cyclo additions with alkynes, alkynes mostly with alkynes and then with alkynes, with the nitrenes.

Then, we will discuss about various type of insertion reaction ok, it could be intramolecular, it could be inter molecular reactions for different type of nitrenes and finally, we will discuss lot of rearrangement reactions ok. As per example, Hofmann rearrangement, Lossen rearrangements, Meet Koteas like different type of rearrangements with nitrenes we will discuss ok.

So, next we will see that the first topic of our nitrenes reactions that is the cyclo addition ok.

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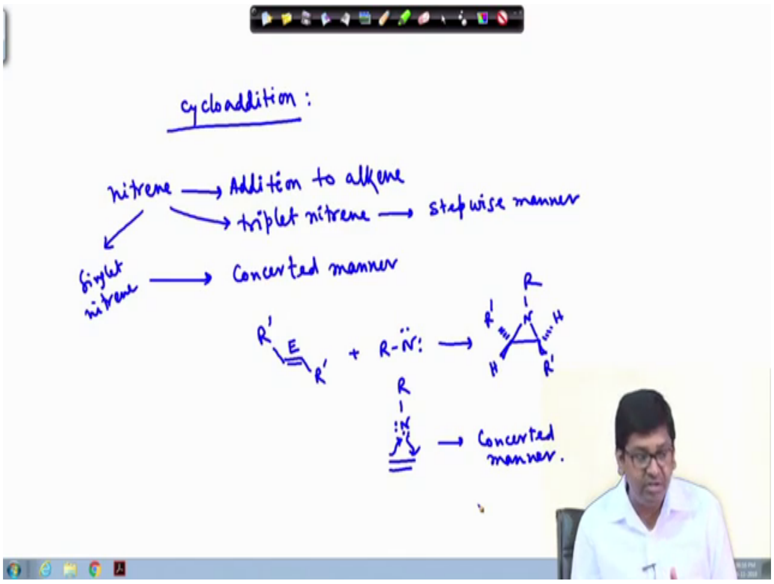

cycloaddition :

nitrene → Addition to alkene

→ triplet nitrene → stepwise manner

singlet nitrene → Concerted manner

So, if you see in case of cycloaddition, this is similar like carbines like nitrenes is generally electrophilic in nature ok. So, mostly it reacts with various type of alkynes, which are in general electron rich that reacts very nicely with different type of nitrenes as these nitrenes are in general electron deficient ok.

So, what they will do in case of triplet nitrene and in place of singlet nitrene? We have seen in case of carbines that if the carbines are singlet in nature, they generally react with the alkynes in concerted manner and if the carbines are triplet in nature then they generally reacts in stepwise manner, we have seen those things. So, in case of nitrenes also it is in similar way, they will react that in case of this nitrenes, if it is a singlet nitrene they will react in concerted manner. So, the retention of stereochemistry of the alkynes will occur where whereas, if the nitrenes are triplet in nature then they will react in stepwise manner and of course, you will get the mixture of c strands products ok.

So, what we have seen that in case of addition to alkene ok. So, nitrenes addition to alkene, if we see that if it is singlet nitrene then it will works like a in a concerted manner ok. Whereas, if the nitrenes triplet nitrene then they will give the in a stepwise manner.

So, stepwise manner basically these triplet nitrene they are actually acting like a diuretical way. So, they will react with the alkynes in a stepwise manner. We have discussed these mechanisms, how this stepwise manner or how these concerted reactions are going through in case of carbine in a very detail way. So, here we will not discuss those things in very detail way, but it is also in similar mode of action, this is also going via a concerted in case of singlet nitrene and in case of triplet nitrene, it is going like a stepwise manner ok.

So, as for example, if we see that if we take ok, so, this is the E olefin. If we take with a singlet nitrene, after this addition reaction, this cyclo addition reaction this is your one to cyclo addition type. So, this will give this type of azetidine product ok. Similarly, if this is cis then you will get the cis product ok. So, if the geometry is z for this olefin you will get cis product.

So, in general the olefin and the corresponding nitrene, they will react in a concerted manner ok. So, they will react in concerted manner. So, the geometry is here retaining that mean retention of this stereochemistry happening ok. So, this is also in similar like carbine hm. Now what we will see that, how different type of alkynes are actually reacting with various type of nitrenes or nitrene type of intermediates reactive intermediates.

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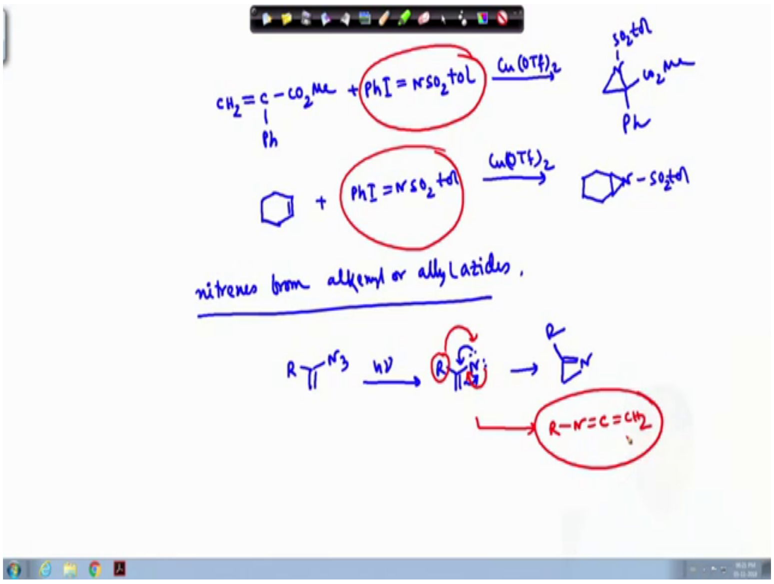

As for example, if we take this olefin, this terminal olefin and if we take this aryl sulfonyl amino iodine, this is like para toluene sulfonium, so, in presence of copper triplet ok. So, that will generate from this one, this is the corresponding arene sulfone amino iodine in here, it is phenol sulfonyl rather this is the iodine that is attached with this paratoluene sulfonyl iodine actually.

So, if this one will react with this corresponding olefin. So, this will give the azetidine ring, this one is corresponding ok. So, this will be the end product fine. Similar way, if we take this olefin cyclohexane here then similarly in presence of this sulfonyl amino iodine that is let us say, we have taken NSO2toline then again in presence of copper triplet ok. So, this will generate from here, this will generate the corresponding or in this case here, this will generate the corresponding nitrene and that eventually will give the end product sorry, the corresponding azetidine ring ok.

So, these are the way that this 1 2 cycloaddition is happening with various type of nitrene species with olefins. Now we will see not only this type of alkynes rather, if the nitrenes that generates from various alkenyl and ally latides, what will be the consequences. So, let us say if this nitrene that is associated with the corresponding olefin in a same molecule; that means, the reaction is going to happen in intramolecular way then what will happen? Obviously, product that is coming from these reactions are highly strained compounds ok.

As for example, if we take the nitrenes from various alkenyl or ally latides then what will happen? First let us say, we have taken this vinyl azide compound and we have under photo lytic condition then this will create this corresponding nitrene ok. Now, this nitrene will give can give 2 different way, 2 different product as per example, if this will migrate over here then actually, this type of highly strained ring will form 3 member nitrogen containing ring will form ok. So, this will generate this type of as a ring type of compounds actually. So, or another option is also there, that is up not only this one rather, this group that can also migrate ok.

So, once this will generate like this. So, this can also migrate ok. So, what we will form? The end product, that will be the corresponding rearranged product that is nothing, but this type of product ok. So, in this case what we will get that finally, this will be the product that when these not only this double bond rather, these R group that will migrate over here then it will give finally, this type of like in case of we have seen that in case of carbines, it gives the corresponding ketene type of compounds. So, here also you will get similar analogous compound ok.

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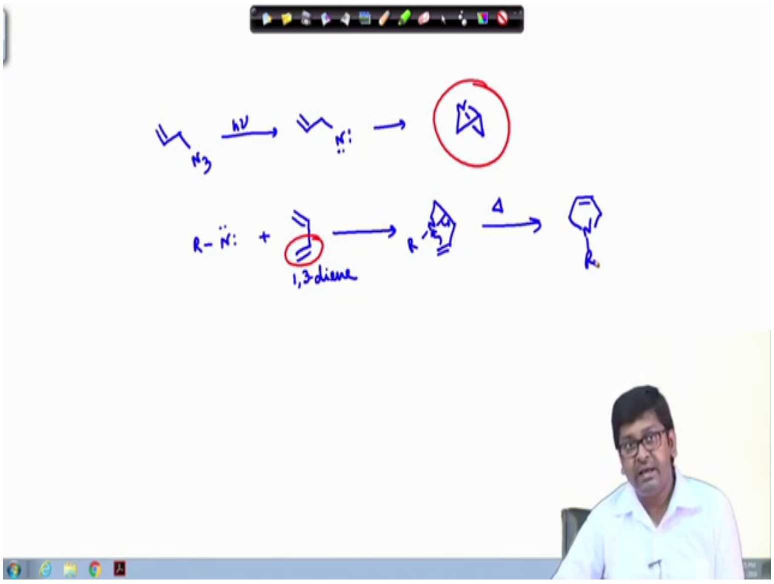

Next what we will see that, if we take the corresponding allyl azides ok.

So, let us say we have taken these ally azides for the precursor of the corresponding nitrene, now again under photoelectric condition. So, this will give the corresponding nitrene ok. Now once, this nitrene generated then now this can nicely give the corresponding cyclo addition product and that is this highly strained compound, where these 3 membered ring remember, this azetidine ring 2 azetidine rings are fused ok.

So, this is highly strained because, if you see this nitrogen that is actually getting addition in this olefin and once it is happening, it is actually giving these 2 strained azetidine ring that is fused together to finally, give this product ok. In similar mode like nitrenes not only with this alkene different type of alkenes or it is reacting it can again react in 1 2 addition mode to 1 3 times also.

So, what I am meaning that let us say, you have 1 3 diene. So, in that case what will be the end product? As per example, let us say we have taken this nitrene and the corresponding 1 3 diene ok. So, if we take this now in this case, if it reacts with the corresponding nitrenes, it actually reacts with the only the 1 2 additions will happen that means this will only react with one of them as per you have we have seen that in case of carbines also it is reacting in the similar mode of fashion. So, here also it will react in similar way that, it will only react with one of this olefin ok.

So, finally, what will be the in this case, the product will be and now under heating condition ok. So, in this case what will give? This will actually give the corresponding dihydro pyrrole moiety by the certain rearrangement ok. So, this will overall give this dihydro pyrrole moiety ok. So, this is the way that nitrene can react with various type of olefins ok, where we have seen that mostly it is also behaving in similar fashion like carbines.

Next we will see that how these nitrenes that is going to react with various alkynes ok. So, we will see now addition to alkynes.

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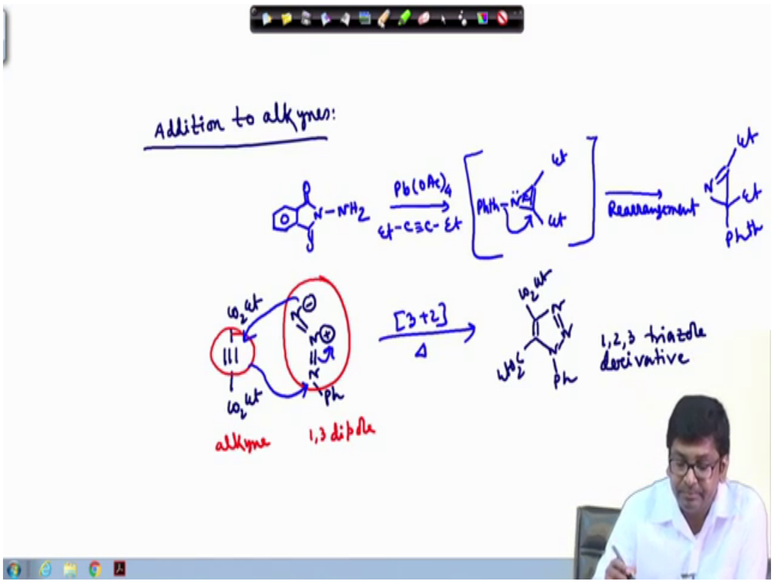

So, we have seen in case of carbines, how they are reacting with alkynes ok. So, in similar way here, nitrenes that is also electron deficient species and that is also similar way that is going to react with the alkynes. As per example, we will see here that first we will take this N amido N aminophthalimide type of species, which after oxidation will give the corresponding nitrate, this N aminophthalimide, this derivative in presence of oxidant ok. So, this can react with this alkyne to give the corresponding azetidine ring ok.

So once, it is having this then; obviously, I am not writing the whole thing. So, basically we can write here Phth, in spite of writing the whole thing and then we have seen that this compound is not stable because, this is basically if you see nitrogen's are having 2 lone pairs and so in this case, this is getting anti aromatic ok. So, if this is becomes anti aromatic then what will happen? This will again rearrange itself ok.

So, due to that rearrangement what will happen that this as azetidine ring will convert into it is analog. So, what will happen here that this is azetidine ring will actually this phthalimide group will migrate over here and this one will sit. So, overall the product will be in this case ok. So, in this case what we will get? We will get the initial product in such a way that, this is not stable product because, this is somewhat anti aromatic and once it, becomes anti aromatic it loses it is stability and after the rearrangement, we are getting these another rearranged azetidine ring and that is nothing, but this particular product ok.

So, what will happen if that that way we are generating like let us say, azides we have taken and alkyne we have taken ok. So, under thermal condition it should give the corresponding nitrene and then that cyclo additions type reaction should occur, but what actually in many cases, it has been found that the reactions of azides and alkynes are so facile that, in spite of giving that nitrene, this azides which is actually on 3 dipole also we can consider them as 1 3 dipole that can react nicely with the alkynes in a 3 plus 2 cyclo additions mode.

So, what I am meaning that if we have let us say this aklyne, now these can have the corresponding this is the azide. So, this is your alkyne this is the alkyne part and this is the azide part. Now, if you see that this is nothing, but 1 3 dipole and this is the alkyne. Now this can nicely goes in 3 plus 2 cycloaddition mode; that means that this can attack like this ok.

So, under thermal conditions before giving the nitrene species, this can rapidly convert to the corresponding 1 2 3 triazole derivative, that is another very important heterocyclic highly enriched nitrogen enriched heterocycle that is called 1 2 3 triazole moiety that we will get. So, what will be the product? Then the product will be ok. So, here this and then N and then CO 2 ut and here CO 2 ut, ok.

So, these are the corresponding 1 2 3 triazole derivative ok. So, in this case, what we have found, in spite of generating the nitrene rather this 1 3 dipole here, it is azide that is nicely going through 3 plus 2 cyclo additions and which finally, gives that without giving the this nitrene based cyclo addition product rather, it is giving the corresponding 1 2 3 triazole derivative ok.

So, overall this is another type of reactions that is actually coming not through nitrogen rather it is precursor that is without generating the nitrogen species that is giving this different type of reactions only what is the reason that in this case? That this 1 3 dipole that azides that reacts very fast under these thermal conditions with the alkynes so, that this triazole moiety can generate ok.

Now, what will happen if we take this type of nitrenes and what will happen when they will react with the corresponding arenes.?

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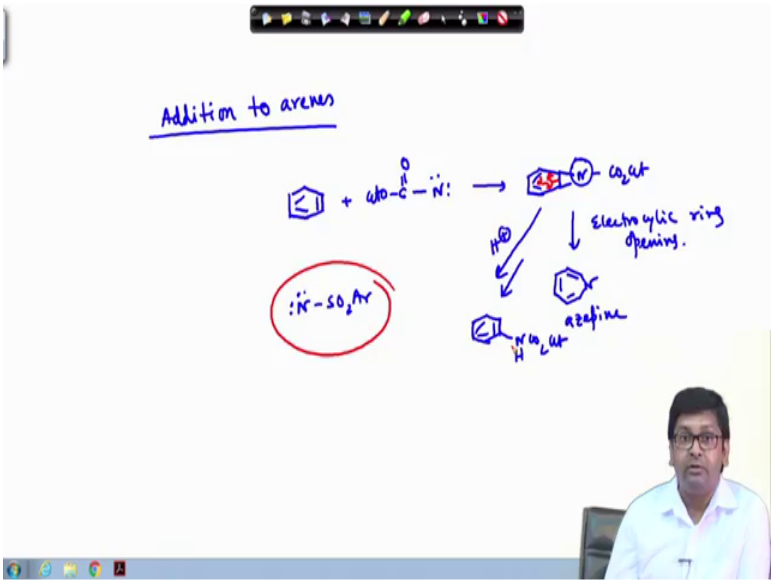

So, what I am meaning to say, that addition to arenes. As per example, this nitrene that can also react with very neutral that is benzene ok. So, this is this will generate, if it reacts with the corresponding benzene the as per example, if you take toxic carbonyl nitrene here ok.

So in this case, this will generate this type of 3 member azetidine type of ring then the corresponding electro cyclic ring opening will happen in this way ok. Once, this electro cyclic ring opening will happen then this will give the 7 member azetidine ring ok. So, 1 2 3 4 5 6 7 alright; so, next ok. So, this is called azetidine ring ok.

So, 7 member nitrogen containing these compounds, this is the azetidine ring ok. So now, once this is having then what will happen? Then these compound actually coming through this first this one to cycloadditions followed by this electro cyclic ring opening. So, electro cyclic ring opening that leads to this azetidine ring, but when these nitrene is associated with aryl sulfonyl group then it has been found that not only this type of azetidine ring is forming. Rather in similar way like here, it has found that in this one if in presence of acid what happens actually that in presence of acids, this will give the corresponding and aniline derivative.

So, the protonations will occur here and once the protonations will occur here this ring will open and after that deprotonation will give the corresponding and aniline derivative ok. So, NH CO 2 et in presence of acid, but if you have this NSO2 Ar in that case, it is not even going through these, you do not need even acid.

In absence of acids also this ring that is that will without going through this electro cyclic ring opening rather as these due to the presence of these sulfonamide group, these can easily open these 3 membered ring in without even in presence of acids. So that finally, you will get this annealing type of derivatives that is very facile in case of these nitrenes that is associated with this aryl sulfonyl group. In that case, this type of aniline derivatives are predominant because of the stability of this anion in presence of NSO2 Ar is very good ok.

Thank you very much.