Reactive Intermediates: Carbene and Nitrene

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Lecture – 17
Nitrene (Contd.)

Hello, everybody. Welcome to my course that is Reactive Intermediates, Carbenes and Nitrenes. We were discussing in my previous class that the importance of nitrenes and their structures and hybridizations, how they will behave in different type of reactions, what are their characteristics and their application part, we have discussed those things.

So, today we will discuss these nitrogen analog of carbene that is nitrenes generation, ok.

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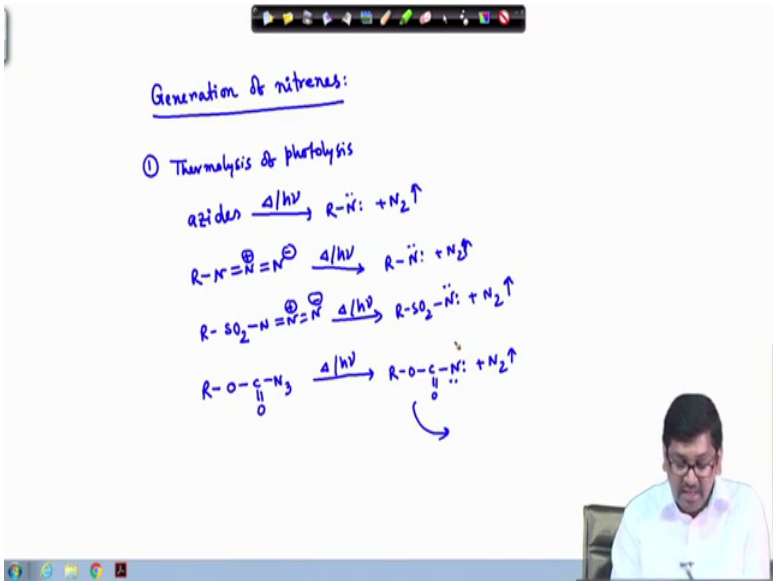

So, what we will discuss generation of nitrenes, ok. We have already mentioned that nitrenes are actually the nitrogen analog of carbenes and they possess almost similar type of structural features characteristics; as for example, like they also having six electrons and they are also short lived species, transient species, ok. So, they also behave in a similar manner like carbenes, but due to having some different structural features they are giving different reactivity in certain cases, ok.

So, in similar like carbenes, now nitrenes also can be generated through various ways. If we see in case of carbenes one of the most used method was to thermal or photo

chemical decomposition of the azo compounds, ok. So, in these case if we wanted to generate now the nitrenes what could be the most used or what could be the first choice that is obviously, in that case like carbenes case we have decomposed that azo compounds. So, nitrogen is eliminated and the carbene that electron deficient carbene species generated.

In this case also, similar way as it is the nitrogen analog of the carbene, so, we can actually go for this thermal or photo chemical decompositions of what of azides, ok. So, first method that could be the thermal thermolysis or we can call or photolysis ok. So, in this case we have to irradiate azides, ok, either heat or h nu depending upon the requirement or reactivity, we can actually generate the corresponding nitrene and what it will liberate? This will liberate the nitrogen.

Now, what is this azides? Azides are nothing, but the species. How we can synthesis this azide, any idea? Ok. So, azides can be nicely synthesised starting from alkyl helides mostly helides could be bromide, chlorides or iodized with these sodium azide as a azide source. If we simply use it, these will give directly the corresponding alkyl or aryl azides. That could be the nice precursor for the generation of nitrene, ok.

So, in these case and how we can detect that azide as formed in the reactions as a starting material because again these could be also nicely detect through IR spectroscopy, ok, Infrared spectroscopy and in these spectro through these spectroscopy actually some stretching frequency particular stretching frequency is their around 2100 centimetre inverse, there if you see that nice peak will come then we can confirm that azide as formed from the corresponding alkyl helide where that band is absent, ok.

So, in these case if we use thermal or photo chemical irradiation then what it will form this will form the nitrene, or this R here could be alkyl or aryl you can take sulfonyl azide, under similar condition this will also give the corresponding nitrene with the nitrogen elimination, ok.

Similarly, if you take alkyl azido formate as a starting material, so, this will also give this carbo alchoxy nitrene, this will generate this carbo alchoxy nitrene with nitrogen elimination. So, in all these cases we can generate though thermal or photo chemical irradiation the required nitrene as a reactive intermediate, and these are all very short lived species which are very much reactive, ok. And, these particular nitrene there it has

been found that these are more selective, ok, more selective in nature then corresponding carbenes.

Carbenes are very reactive most of the cases they are inserting in non-selective manner ok, but these particular nitrenes it has been found that is pretty nicely it can give lot of selective reactions. However, apart from these thermal or photo chemical decomposition the azides can be converted into its nitrene through the nitrogen liberation in presence of transition metal salts, ok; so, that also possible apart from these cases, ok.

So, these decomposition of these azide that in presence of transition metal salts also give nitrenes and actually it has been it has been explored in various ways in recent days that these nitrenes can be actually inserted into lot of active bi-active molecules in their lateral stage, I mean that is having various type of functional groups among that also it can be selectively inserted into certain position of these complex molecules and that way this transition metal transition metal salts are nowadays very important to generate this type of nitrenes, ok.

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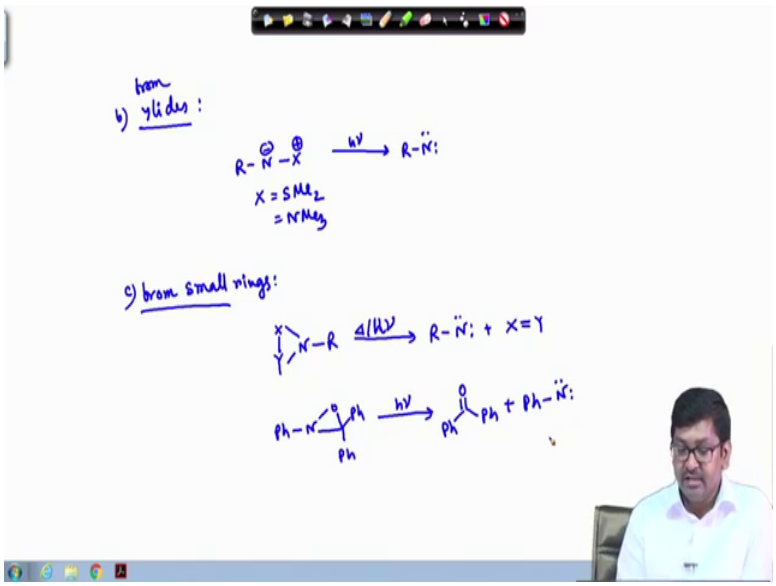

Another way that nitrenes can be generated from that is called ylides, ok. So, first we have seen that from the azides next it will be from ylides. You can give this as b, that is a, from ylides. So, from ylides so, if we take these are not that common like a carbon its carbon counterpart, but there are possibility that and here x could be SMe 2 or NMe 3. So, they are actually giving this type of ylides and these are called imino phosphorane or

imino sulfurin and these imino phosphorane or imino sulfurin in presence of h nu actually gives that corresponding nitrene, ok. We will see later many examples with those things.

Another precursor for the synthesis of these nitrene species could be the small rings; so, from so, from small rings, ok. In case of carbenes we have seen that if there is small rings like epoxide kinds of things that can be actually converted into the carbenes under thermal or photo chemical irradiations. Similarly, here if we have this type of ring as per example here X, Y we can write like this under thermal or photo chemical conditions that gives the nitrene plus some small molecule will be eliminated, ok.

If we take oxaziridine as per example as a precursor for generation of nitrene through this way under photo chemical irradiation this oxide regime ring will generate one small keto compound plus the corresponding nitrene, ok. So, there are three ways that we have so far discussed one is from the azides, that is very common or very famous then the nitrenes can be generated through ylides or they can be generated from various small rings through the decomposition of that small rings leads to the corresponding nitrene and the elimination of some small molecules.

In these case this oxide regime ring gives the corresponding keto compound as a small molecules these benzophenone type of molecules and here this nitrene that has been generated as the reactive intermediate, ok.

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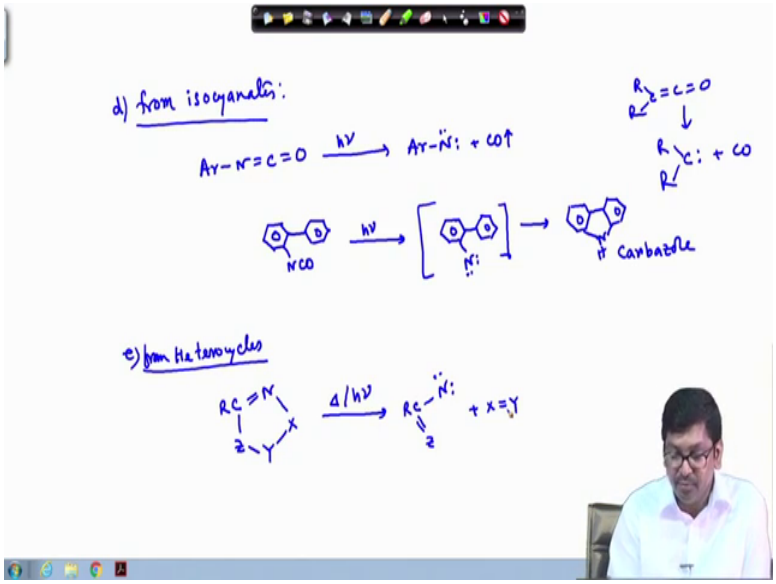

Next, these nitrenes another method this can be generated from isocyanates. We have seen in case of carbenes when we have generated the carbenes from wanted to generated carbenes from similar cases what we have taken as a precursor? Yes, we have taken that precursor as the ketenes, ok.

As for example, what we have taken there that, ok. So from there we got this ok, for the carbene. So, in case of nitrenes what will be that in that case yes? Yes, you are correct that is from the isocyanates. I am sorry, from isocyanates ok. So, isocyanates means the structure you can think about the ketenes then isocyanates this under now photo chemical irradiation. So, this will give the corresponding nitrene plus carbon monoxide elimination, and this will be generated here nitrene in a similar or analogous way of generating carbene from the ketenes here also in similar conditions this will be giving the required nitrene species, ok.

As for example, take this particular isocyanate under photo chemical irradiation, what has formed? So, this has formed; the corresponding carbazole moiety through the generation of this nitrene species, ok. So, what it has generated? So, this as generated one very important nitrogen containing heterocycles that is called carbazole. So, this is the carbazol moiety that can be generated from these isocyanate precursors under the photo chemical irradiation, ok.

Similarly, another method is there through that we can generate the nitrene precursor and nowadays it becomes very popular due to it is easy handling as the azides are what we what we said that azides are most common and useful, but lot of cases azides are very hazardous and they are explosives also, and after certain temperature most of this azides that decomposing and they can explored. So, there are some potential there potential limitations are there for this azides. So, in that case this various techniques to generate nitrenes as involved because of this various problems with the azide compounds and they are first decompositions actually leads to develop various our sources of for generation of the nitrenes.

As for example, if we take this heterocycles so, from heterocycles. So, take this heterocycle, under thermal or photo chemical irradiations this can again eliminate a small molecule and give the required nitrene species, ok. So, these are the way that from from heterocycles also we can generate the required nitrene species, ok.

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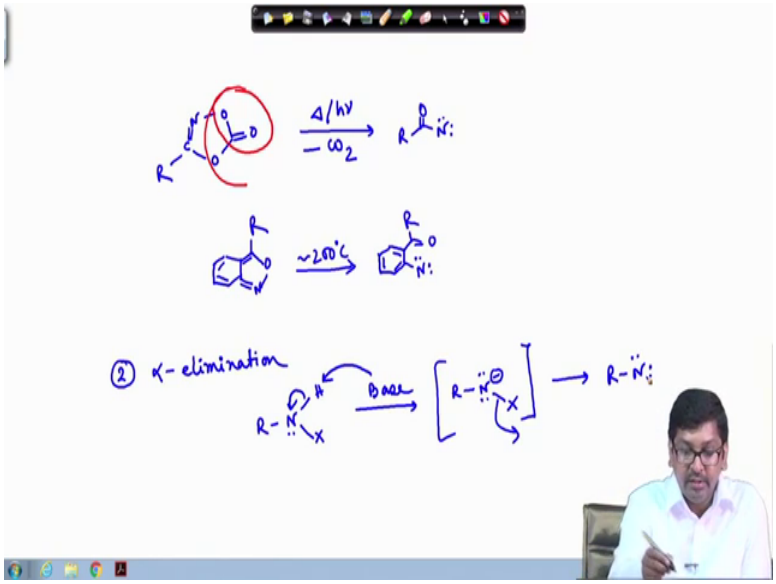

As per example if you take some oxazole moiety that is 1 for 2 diocxazole pione this is the 1 for 2 dioxazine pione moiety and if we under thermal or photo chemical conditions actually this will liberate the carbon dioxide, sorry. This will liberate this carbon dioxide moiety to give the corresponding nitrene, ok. So, this particular way we can liberate the carbon dioxide and then generate this acyl nitrene moiety, ok.

Another similar heterocycle that is this anthranil type of moiety under high temperature or under transition material salts, it can give the corresponding nitrene moiety and this could be used for aryl amination of various substrates, ok. So, nitrene is generated, now this nitrene can be used for various type of reactions; importantly, here it is the phenyl nitrene or aryl nitrene that has been generated, ok.

We have discussed previously also that not only these through these thermolysis or photolysis there are other method that can also leads to the carbine. We have discussed in case of carbenes; as for examples alpha eliminations. In this case also we can think that alpha elimination can provide the required nitrene, ok. So, if we take this particular substrate and treat it with this we have seen in case of carbene also if we at use this depending upon the basic strength. So, that could be used to deprotonate and then the elimination of that living group here it could be halides, it could be other living group also.

So, in presence of this if that will pick up this, then obviously, now the alpha elimination that will lead to the corresponding nitrene ok. So, this is another technique apart from the apart from the thermal or photo thermolysis or photolysis of the azides this is another way that alpha elimination can be done to get the required nitrene moiety, ok.

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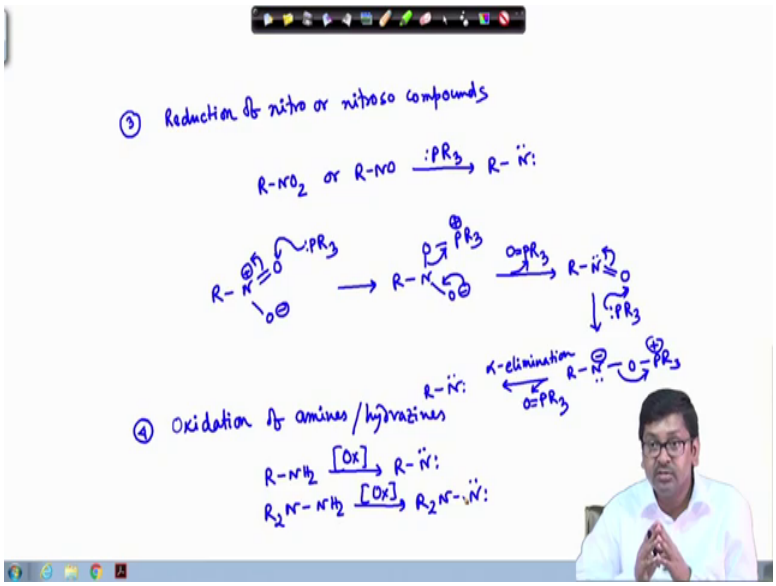

Not only that another method is also there, this is called the reduction of nitro or nitroso compound that can also lead to generate the required nitrene moiety. So, reduction of nitro or nitroso compounds. As per example, if we take this or nitroso compound in presence of some phosphines this will give the corresponding nitrene, ok. So, what will happen if you see the mechanism how does it work? So, we have this is our nitro compound, ok. So, now, we have this phosphine. So, this can attack, ok. So, what we will get? Ok. So, now, this can go back and as phosphorous and oxygen having very affinity towards. So, this bond will clip and will get this phosphine ozide, ok.

So, once it will be eliminated then what it will form? It will form the corresponding nitroso and once you have this nitroso then again in presence of phosphine, ok. And, now the alpha elimination again due to the affinity towards this phosphorous oxygen bonds, ok. So now, what it will form this will generate the corresponding nitrene moiety through the, ok.

So, what we have seen, that we have seen not only the thermolysis or photolysis of azides which is very common method not only that other methods also similarly

important, either it is by the different type of formation of nitrenes from different type of heterolysis of sorry from hetero different type of heterocycle through the thermolysis or photolysis or it could be the alpha elimination or it could be the reduction of nitro or nitroso compounds.

Similarly, another method also there that is I have already shown once that when we have discussed the stable nitrene compound which is possible to detect that there we have mentioned that hydrogen type of moieties also can be oxidized to get the nitrenes, ok. So, that way we will also discuss that there is another method that is called oxidation, amines or hydrazines, ok. So, if we take amines and in presence of some oxidant, this will give the nitrene or hydrazine moiety that is also in presence of oxidant will give certain nitrenes, ok.

So, far what we have discussed? We have discussed the various generous technique of generating the nitrene moiety, it is not only the photolysis or thermolysis of azides, but also we can generate those nitrenes from various small molecules, heterocycles or from the alpha eliminations or from reduction of nitro or nitroso compounds and could be oxidations of amines or hydrazines.

So, these processes has been evolved due to the certain certain problems with various azides due to their due to their stability problem as it can explored very fast, as it can explored after certain temperatures and most of this azides are also not very stable moiety. So, handling of those azides also pretty difficult; so, with aspect actually these different type of techniques has been evolved due to various applications.

Next class we will discuss the different reactions of nitrenes, ok.

Thank you.