Reactive Intermediates: Carbene and Nitrene
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Lecture – 14
Reaction of Carbene (Contd.)

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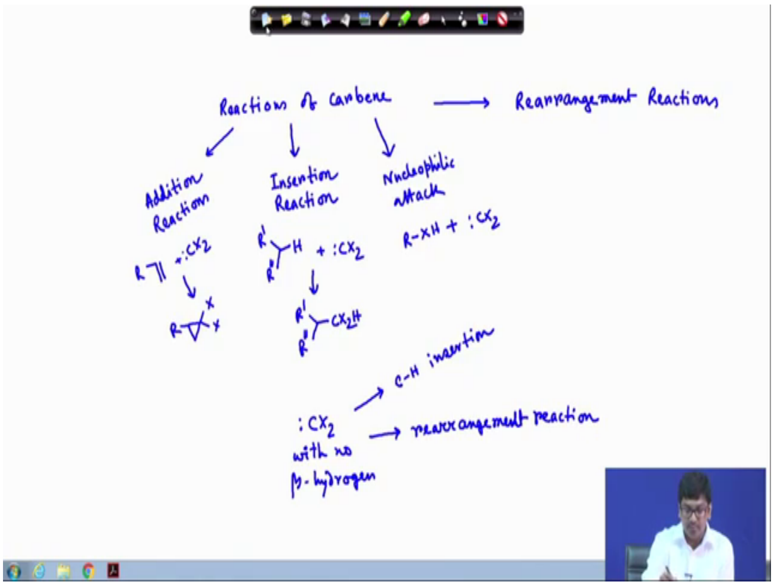

Hello everybody. Welcome to my course Reactive Intermediates, Carbenes and Nitrenes. So far we have learned various aspects of carbenes. Now, we are studying among the different reactions that is associated with carbenes. So, so far what we have learned that among the carbene reactions, first we have learned the addition reactions ok. So, what we have learned over there if there is some kind of olefin or alkyne, then this will give some cyclopropene ring ok.

Next we have learned about insertion reactions ok. What does it mean that if there is some carbenes is there, and there is some as for example some carbon hydrogen bonds is there, these carbene can be inserted into that carbon hydrogen bond. As for example, so these can give ok. So, another type of reactions also we have learned in the last class that is the nucleophilic attack of various nucleophiles towards the carbene. As for example, if you have R-XH, that can react with the corresponding carbene to give the nucleophilic attack product ok.

So, now next what today we will learn another type of reaction that is called rearrangement reactions ok. So, if we see that if there are certain substrates with no beta hydrogens, I mean the carbenes that it generated, there is no beta hydrogens. So, there are various type of reactions are possible. As for example, there C-H insertion reactions are possible as well as their the rearrangement reactions also possible. So, if we have this carbene with no beta hydrogen, then there is high possibility of C-H insertion ok. Additionally, these can proceed with rearrangement reaction ok.

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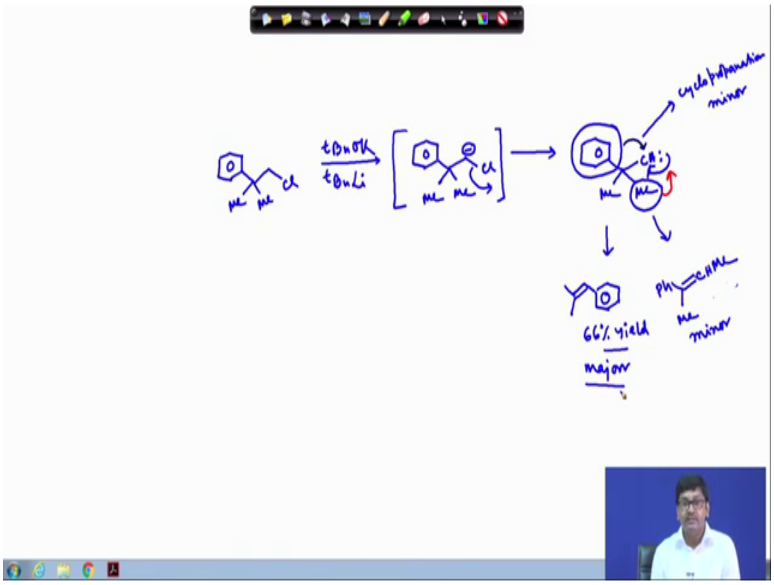

If we take this substrate, where there is no beta hydrogen. Now, in presence of slossures one of the slossures base, we know previously that it will generate the carbene moiety through this way, and then the chloride liberation, and then this will give the corresponding carbene. Now, if we see this carbene there are several things possible, as for example there are this C-H insertions that is possible to give some kind of cyclopropanation or there are now two possibility for rearrangement. One is that these methyl can migrate, and this phenyl group can migrate to give the rearranged product.

So, what it will form? It will form actually that once this will come then either this one can migrate or if this one migrate, then another product will form ok. So, now if this one migrates, then what will happen, what will be the product? Then if this phenyl migrates, then the product will be this. And what has been found, this is in 66 percent here that means, this is the major product.

Whereas, if this methyl that can migrate, then obviously what will be form ok. So, in these case what has been found, this is very minor amount, this is also minor, whereas this one is the major product, now question if why it is happening ok. So now, why this one is forming as a major product? If we see the migrating aptitude, the phenyl ring is having more migrating aptitude, then the methyl group or alkyl group that is why here, these migration of these phenyl is move.

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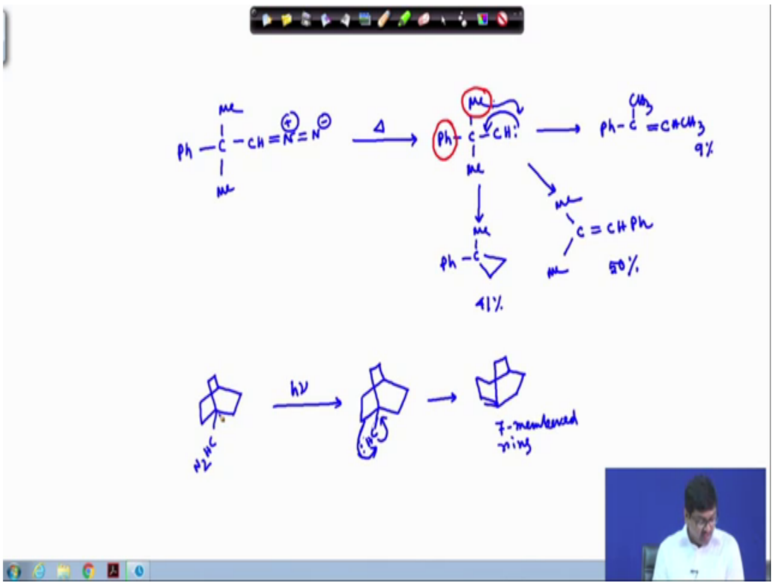

Next, we will see another similar type of example that is here the precursor is the corresponding diazo compound ok. Now, under thermal condition ok, so this will give the corresponding carbene. Now, once this carbene is there, again there is two possibilities or rather three possibilities that first the cyclopropanation can happen as there is no beta hydrogen. So, the cyclopropanation can possible or there are two groups, two rings that is there sorry two groups are there like methyl or phenyl, they can migrate to give the rearranged product.

Let us see what will happen. So, what has been actually found that there is actually this product formed in 41 percent that is the cyclopropanation one, where this insertion happened. Whereas, there are other two products formed by this rearrangement that is the coming of these group or these group whatever it may be ok. So, if this migrates, then the following product will be but this is only 9 percent.

Whereas, the major product that is after the phenyl migration, and that is this product and the yield is 50 percent. So, if you see that where there are different type of reactions are possible, in these type of particular substrates where these beta hydrogen is absent, and actually it gives the mixture of products. And in that case we are getting the as we expected that cyclopropanation happened.

And there is possibility of migration and as there are two different type of groups, which can migrate through this for this rearrangement. So, it is actually possible to see that these two groups actually migrating. And in one case, if the phenyl groups migrating aptitude is higher than the methyl group that is why, phenyl group is migrating and giving the more amount of product, whereas when the methyl group is migrating the amount of product is less because of their difference in the migrating aptitude ok.

In another type of substrates where, again the diazo compounds are the precursor of the carbenes. So, this is a corresponding bicycle, octile diazo methane type of compound ok, this is having the bridged, and now this is the substrate. Under photolysis this can give the corresponding carbene ok.

Now, once this carbene generated, again I am now considering on the major product. So, then this bond can migrate over here or you can draw in this way ok. So, once this will do this migration, then actually the expansion of ring will happen. So, here it is 6 membered ring. So, once this rearrangement happens, then we can make it more clear or more visible here in these way ok.

So, if this happens the due to this rearrangement, the this rings 6 membered ring becomes the 7 membered ring. So, what will be the product, here the product will be ok. So, number of rings if you see that 1, 2, 3, 4, 5, 6, 7, so this becomes the 7 membered ring. So, we are started from 6 membered ring having this bridged, and that we arrive at 7 membered ring again, this is due to this particular rearrangement ok.

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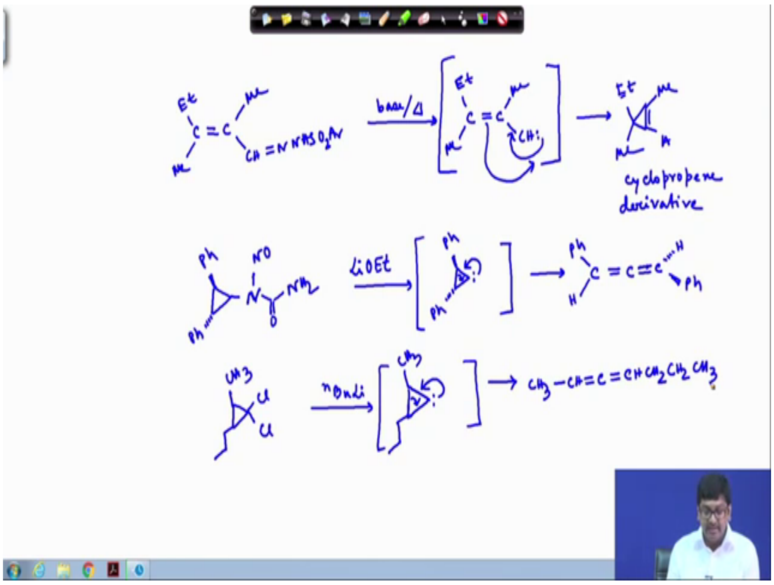

Now, where the carbene that is generated by this under basic medium or under heating condition by any means, if there is a double-bond adjacent to the carbene, then what will happen we will see that example as for example here if we take these carbene, which is adjacent to this. So now this is they this is the carbene precursor, which under basic medium and heating condition that will generate the carbene ok.

So, if we start from this (Refer Time: 15:56) hydrazone and from there if we treat with under basic conditions and heating condition, then that will generate the carbene that actually adjacent to a olefin. Now, once we have this olefin, now it is ready for this rearrangement, and that actually can give this cyclopropene cyclopropene derivative rather so what we will get here, the product that will be ok. So, this is the corresponding cyclopropene derivative ok.

So, we are starting from the (Refer Time: 17:01) hydrazone derivative and or not only (Refer Time: 17:04) this type of it could be air. So, if we treat it with base followed by hitting, then we will generate this carbene. And once this carbene will generated, then that can go for this rearrangement to give the cyclopropene derivative ok.

Next, we will see that if we will generate different type of cyclopropene leadiants, then how that can rearrange to another class of products that is called aleens. As for example if you take this substrate, which is having this cyclopropene ring, so N-nitrosourea type of derivative if we take, then this n nitrosourea type of derivative if we take and treat with some base, then again this will generate, we have seen that different procedure, how we can generate the carbene ok. There also we have seen that how these N-nitrosourea derivative can generate or form the carbene. So, these are the things that are very good precursor for the carbene.

So, here also we have taken the similar type of substrates, where these substrate these N-nitrosourea can be treated with base to form the corresponding carbene. As for example here, we have generated these carbene. Now, these one these carbene is ready for the corresponding rearrangement. So, again we can do this, and this one can come like this. So, if we see that these particular cyclopropene ring now, opened and give the corresponding allene moiety. You know what is allene, in case of allene these two groups and these two groups, they will be perpendicular ok. So, they will not be in a same plane, so that is why they are written in this way. So, this is a special type of compound, this is called allene ok.

In another example of making such kind of allenes, where we have not taken that as a carbene precursor, we have not taken this N-nitrosourea rather we have taken these dichloro substrate ok, this cyclopropene with this dichloro. And now if we treat with n-butyl lithium, then again we as per our previous experience we know that it will give the corresponding carbene ok.

Now, this is ready for the rearrangement. And once it will rearrange, then it will give the desire allene type product, and here it will be these allene ok. So, once we have taking this cyclopropene derivative, which can generated this carbenes that is the cyclopropene (Refer Time: 21:31) rather, so that will whose via this rearrangement to provide this allene substrates ok.

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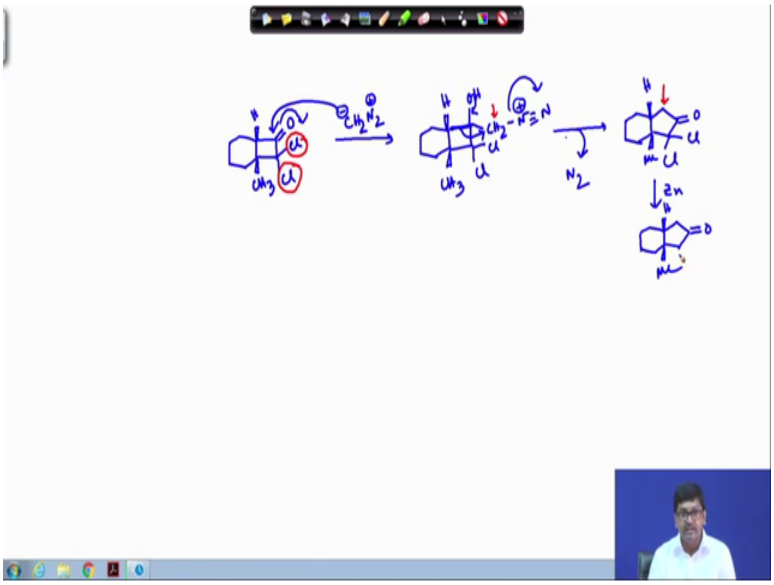

Question is that if we now take another similar type of compound, where these not we are taking the 3 membered cyclopropene ring, rather we have taken the 4 membered ring. Let us see how it will work. So, we have taken this bicyclic compound, where this 6 membered cyclohexane ring is fused with cyclobutanone. And they have this CH 3 junction ok, so this is the substrate.

Now, we know that these substrate if we now treat with the corresponding diazo methane, then what will happen ok. So, now this can nicely react with this because of having these two chloro group, they are having this minus i effect that made these carbonyl group is more electrophilic, these carbonyl center becomes more delta positive ok.

So, this place becomes more electrophilic. So, the diazo methane can react over there, and to give us this product sorry this intermediate that is ok. Now, once it is there, then this can nicely migrate over this for the nitrogen elimination. And if you see carefully, you can understand that here 4 membered ring can be expanded to 5 membered ring right so ok. So, now once this bond, these one migrated to these particular carbon, then if we see this is this carbon what is here, so now it is here ok.

So, then the carbonyl group, because this bond is breaking right and here that is making the new bond with these particular carbon, and giving the corresponding 6-5 fused ring with dichloro ok. Now, this dichloro that can be in presence of zinc can give the situation of this ring to a in presence of zinc, these compound becomes the saturated ring, and with the that reduction happens and then that that gives this corresponding 6-5 fused compound ok. So, these are different type of rearrangement reactions that we have discussed now ok.

Thank you.