Reactive Intermediates: Carbene and Nitrene
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Lecture – 06
Generation of Carbene (Contd.)

Welcome everybody. So now, in this class we will continue the Generation of the Carbene this topic. In the last class we have discussed about the generation of the carbene from the diazomethane by the decomposition through the heat or under photochemical condition. After that we have learnt that how the carbenes can be synthesized from the diazocarbonyl compounds and obviously the synthesis of the diazocarbonyl compounds also.

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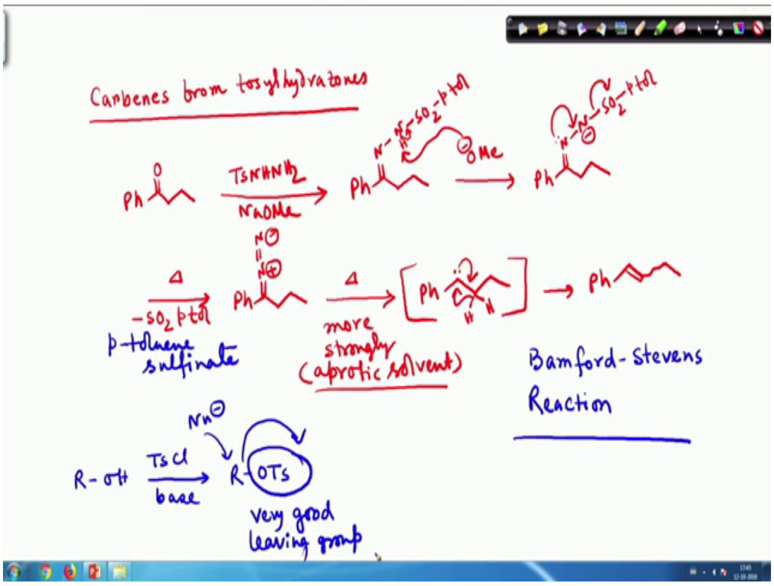

Now, we will learn in another method of carbene preparation that is carbenes from tosylhydrazones. So, here the carbenes will generate as an reacting intermediate of the reaction not as a starting material; what does it mean that we have these keto compound and if will use this reagent in presence of base that tosyl derivative of this hydrogen then that will keep the corresponding tosylhydrazone moiety. I am writing in place of tosyl this para toluenesulfonyl, ok.

So now, we have this base which will pick up this proton, ok. Once this will pick up, this will give the corresponding derivative anionic derivative ok. So now, we have this lone pairs here, ok. So, here this will come and this will eliminate. So, what we will get over here under heating condition this will eliminate this para toluenesulfinate group and will give here the corresponding diazo compound that is ok. Here I would like to mention one thing that in general when we have learnt the living group things what we have used to do that let us say we have R OH we use tosyl chloride and some base, ok. So, what we prepare R O tosyl or para toluenesulfonyl group, ok.

So, now this is considered as a very good leaving group, because if you put some nucleophile it will attack over here and this will go. But, in this case you see there is a very unusual or uncommon leaving group that is eliminating to generate this diazo compound, ok. So, that is nothing, but this is called para toluene sulfinate, ok. But, what we previously knew that para toluenesulfonate that is the better leaving group, but here what is the leaving group here it is leaving group is para toluenesulfinate group, ok. So, that gives our desire diazo compound, ok. So, it is important to remember here this is not the para toluene sulphonate group rather this is para toluene sufinate group, ok.

Now, under heating conditions what will happen? Now under heating condition or more strongly heating condition more strong heating condition so, the nitrogen will eliminate and definitely this is in aprotic solvent I am talking about because in protic solvent the reactions will work in different way that will generate some carbenium carbenium ion, but in these case this will give the corresponding carbene in aprotic solvent, this is important aprotic solvent, ok.

So, this will generate the corresponding carbene and now this carbene will react in this way to give the corresponding olefin, ok. This is the mixture of olefin it will form and this is called this is a name reaction this is called Bamford-Steven reaction. What it is called? Bamford-Steven’s reaction.

So, here this will give such kind of olefin which is a mixture of e and z and that will give this Bamford-Steven’s reactions. We will learn many reactions or applications of this Bamford-Steven’s reactions and we will see many new reaction or new applications in later stage of this course, ok.

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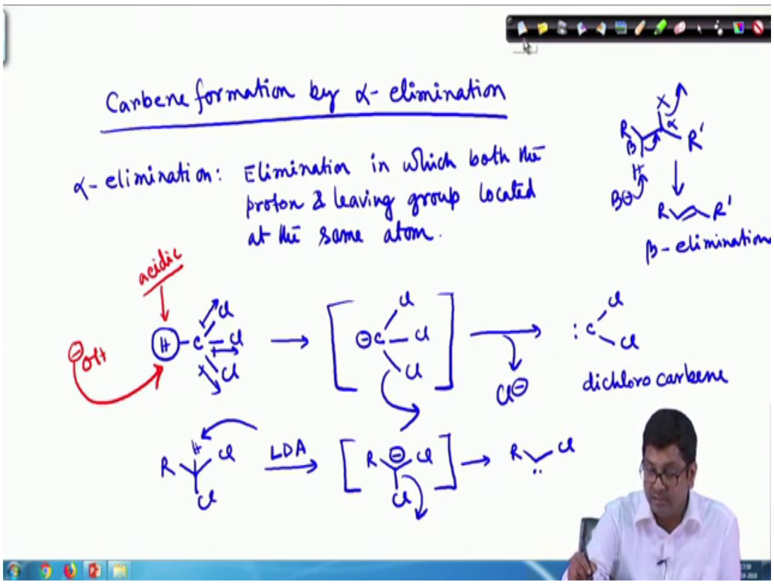

Carbene formation by α- elimination

α- elimination: Elimination in which both the proton & leaving group located at the same atom.

Next we will see the carbene formation from or via alpha elimination. So, another technique of carbene generation that is called carbene formation by alpha-elimination; so before that we have to learn what is alpha elimination. Do you know; what is beta elimination? We have learnt this, ok. When we have studied in the first year that elimination reactions we have learned about this beta elimination.

I am just showing inside some kind of as per example like this. So, you have hydrogen let us say you have R prime something like this or then you have base it is picking up this and this hydrogen and it will give you the corresponding olefin, ok. So, now, this is the let us say alpha this is the beta, ok. So, this is called beta elimination this is the beta elimination. So, here we need to know the alpha elimination, right.

So, what is alpha elimination? Elimination in which the proton and the leaving group both are located in a same atom, that is called alpha elimination, ok; so elimination in which both the proton and leaving group located at the same atom. Here we will see that both this proton and the leaving group are actually located at the same carbon atom. As per example if we take chloroform, and due to this inductive effect of this three chlorine atom minus I effect rather this is pretty acidic. So, this proton is pretty acidic. So, this is acidic proton, ok. So now, base can easily picked up this proton, ok, to generate the corresponding anion, ok. So now, from here chlorine can liberate as a leaving group and once it will liberate from these anion this will generate the corresponding dichloro carbene.

So, this is the dichloro carbene this is one of the very common reaction to generate such kind of dicholoro carbine. Similarly we can use its dichloro derivative as per example like this, but here obviously, you need more strong base because there you have three chlorine atom attached to this carbon atom or carbon centre, but here there are only two chlorine atom. So, you need more strong base as per example we have used here LDA, ok. What is LDA? Lithium di-isopropyl amine that is one base; so this is a very strong base; once you will use that; so, that will pick up this proton and generate these corresponding anion. And once it will generate this will give the corresponding carbine, ok.

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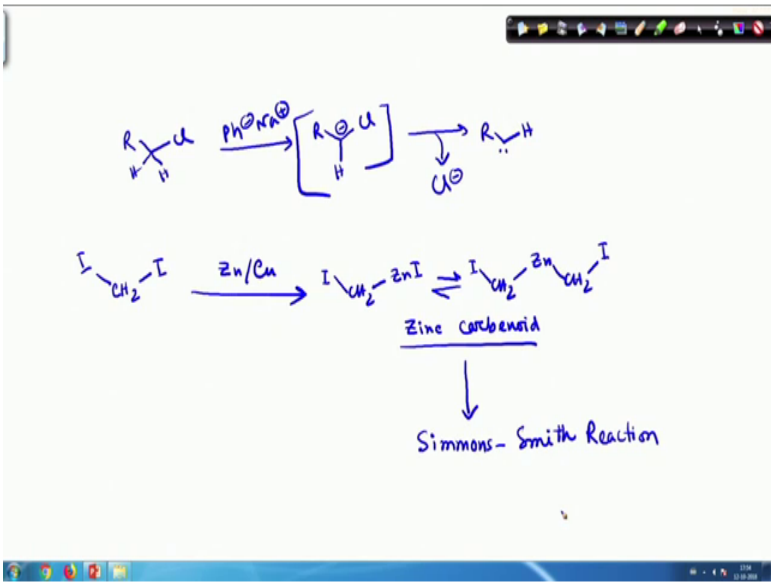

Similarly, if we use the monochloro derivative, that also can generate the carbenes. How? Only thing is that here irrespective of previous way there are less number of chlorine atom. So, these hydrogens are not that much acidic like previous way only thing is that here we have to use more stronger base. So, as per example here we have used this base, and this will generate the corresponding anion and after liberation of chloride. So, this will give the corresponding carbine, ok. So, in these way starting from these chloro derivatives we can synthesize the corresponding carbenes.

In another way if we use diiodomethane in presence of zinc copper couple this can give this zinc compound and then this will give these zinc carbenoid basically and it can stay like this way also ok. So, these are called zinc carbenoid. We have learnt that what is carbene and what carbenoid. So, in this case the metal is the zinc one. So, here that will give this corresponding zinc carbenoids and this has been used enormously in a very well known and famous reaction that is called Simmon's-Smith reaction Simmon's-Smith reaction.

Obviously we will learn many applications of this particular reaction in our later stage when we will learn the reactions and rearrangement of carbenes that time we will specifically go through this particular reactions also that is called Simmon's Smith reactions. Now, so far whatever these carbene generation we have shown that most of the cases what we found that we need the base to generate the carbonyl and then that will by leaving something or some group that gives the corresponding carbene.

Now, if the compound that is going to react with this carbene if that is base sensitive what will happen? So, we are generating in situ because carbenes anyway you cannot store or you cannot basically use it for other purpose rather what we have to do. We have to generate it immediately and then we have to use it, ok. So, for that what we have to use that when you are starting material or some of your substrates of choice you want to react with carbine, if that substrates of choice is base sensitive then what will happen?

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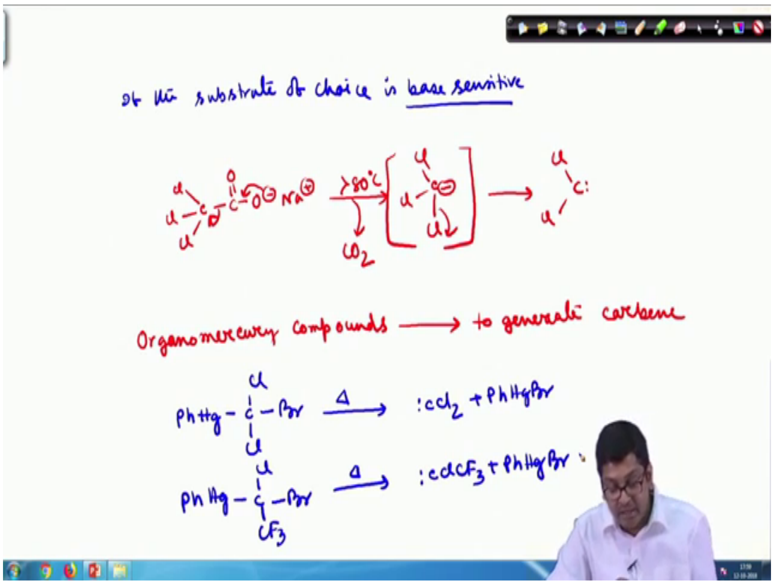

If the substrate of choice is base sensitive

Organomercury compounds ⟶ to generate carbene

In that case definitely we cannot use those techniques rather if the substrate of choice; we can write substrate of choice choice is base sensitive what will happen ok. So, in that case the carbene has to be generated in absence of base ok. Otherwise that base can destroy our substrate. So, over all the reactions will not occur, ok. So, in that case what we will do let us say here the carbene can be generated from these carboxylate also by decomposition of this carboxylate just by heating this will liberate the carbon dioxide. And this sodium trichloroacetate this compound called sodium trichloroacetate that will liberate the corresponding carbon dioxide.

And, once that will liberate the carbon dioxide what that will generate that will generate this trichloro based carbonion and one this trichloro based carbonion generated so, that actually can easily give these dichlorocarbene which we need. See here we have not used any base to synthesize this carbine, ok. So, in this case we can avoid the use of base so that our deserved reaction should happen.

In another way we can use the organomercury compounds for the preparation of the carbenes, ok. So, these can be also used to generate carbene. How? That let us say as per example we can take, ok. This type of substrate if we see this carbon mercury bond that is more covalent than the carbon lithium or other carbon metal bond; in these case what we will do that we will simply go for thermal decomposition. And one we will do the thermal decompositions this will simply generate these dichloro carbene with this molecule PhHgBr, fine.

Similarly, in another case we use this particular compound in presence of chlorine this CF 3 group that also under heating condition will generate this carbene with similar phenyl HgBr. So from organomercury compounds also we can easily synthesize this kind of carbenes in absence of base. So, these are the ways that we can synthesize the carbenes without base presence, ok.

Next is that in another way we can synthesize very stable carbenes, ok. We have learned about this persistent carbenes there we came to know that these type of carbenes even sometimes stable and isolable. So, we will learn how this type of carbenes can be synthesized.

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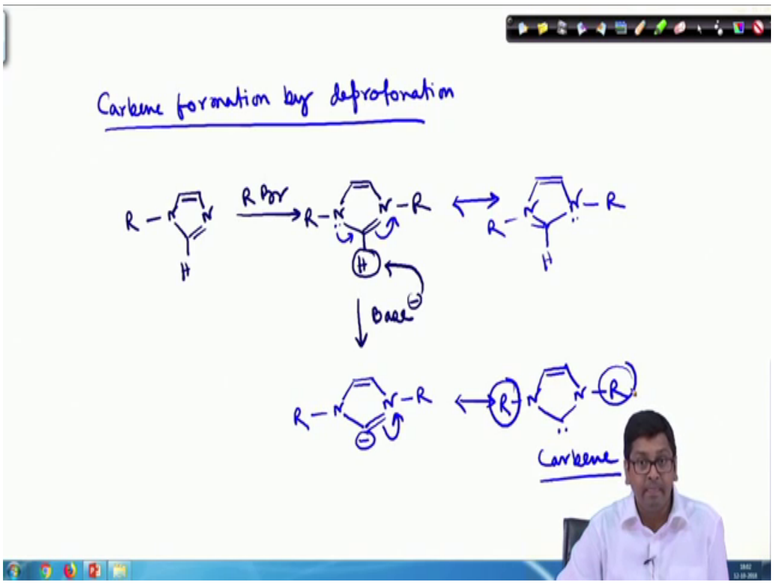

So, carbenes formation by deprotonation. So, this type of carbenes can be synthesized from these from it is corresponding n heterocycles via the deprotonationas. As per example we can see that we have this imidazole moiety and ok. So, in presence of alkyl halide this will again give corresponding dialkylated product, ok. Now, this is acidic proton if you use the base that will pick up this proton and ones that will pick up then what will happen then that will actually generate the corresponding anion, and you have this will have this, ok.

Now, these can stays like a carbene ok. So, these are the corresponding carbenes now these can be also in resonance, ok. So, another resonance structure ok. So, these are the carbenes that we can generate through the deprotonations, ok. These are called n heterocyclic carbenes and we have seen it is enormous use in recent days in various type of transformations, because of it is stability because of its versatility. If you see this R-groups you can actually play around these R-groups and even you can go for this various asymmetric reactions using this in N-heterocyclic carbenes, ok. Lot of enhancive selective reactions also you can use. If you use here all these chiral here this chiral part then you can actually go for various asymmetric synthesis, ok.

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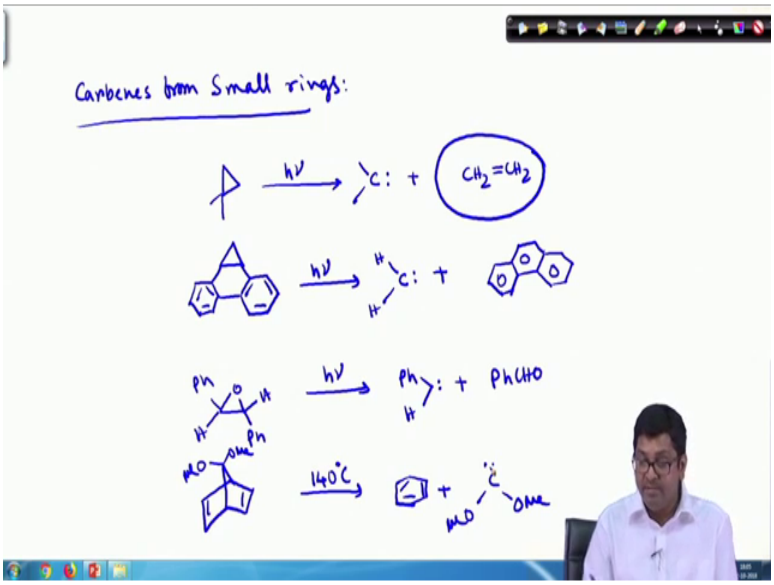

Now, the next is that the synthesis of this carbenes from small rings; so carbenes from small rings. So, if some rings that are small, that are in general strain rings especially if you take the all the three member rings they are very straight. So, under heating or photochemical conditions that generates the carbene at the corresponding stable fragment. So, this is important that after the decomposition that small rings has to give some stable fragment so that it can generate the corresponding carbenes.

As per example if you take this cyclopropane moiety under photochemical decomposition this will give the corresponding carbene plus the stable fragment that is this ethylene. Similarly, if you take this substrate this dihydro phenom 3 type of substrate with the corresponding cycloprapane ring under photochemical decomposition again this will give the corresponding carbine, with the phenon 3 moiety, ok.

Similarly, if we take the corresponding epoxide under similar type of photochemical decomposition it will give the corresponding carbene with benzaldehyde adjustable fragment. And for norbonodyl kital derivate also gives under thermal decomposition keep this stable benzene plus dimethoxy carbine, ok.

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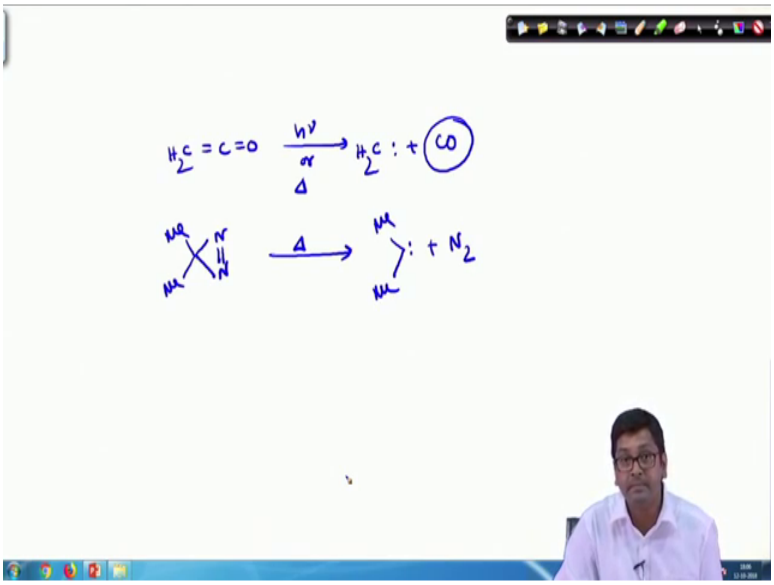

Similarly, like ketene type of moiety also under photochemical or thermal decomposition will give the carbene plus carbon monoxide elimination gives this carbine. Here this is also stable fragment, stable molecule. And similarly decomposition of diacelene rings that also gives under thermal decomposition give this carbene moiety with the nitrogen elimination, ok.

With this, thank you all for today’s lecture.