Reactive Intermediates: Carbene and Nitrene
Prof. Rajarshi Samanta
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 04
Generation of Carbene

Hello everybody. So, in the last class we have learnt that which type of carbenes will be remain as triplet and which type of carbenes will be remain and singlets at their ground state. And after that we have started that that is called persistent carbine; in the last class we have discussed little bit about this persistent carbene or stable carbene.

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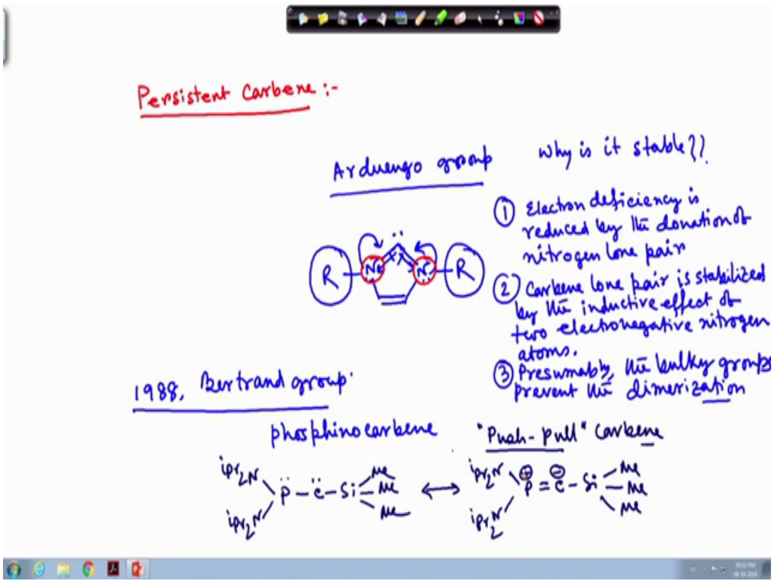

Persistent Carbene :-

Arduengo group

why is it stable??

① Electron deficiency is reduced by the donation of nitrogen lone pair

② Carbene lone pair is stabilized by the inductive effect of two electronegative nitrogen atoms.

③ Presumably, the bulky groups prevent the dimerization

1988, Bertrand group

phosphino carbene

"Push-pull" carbene

We have discussed that this type of carbenes they are stable and they actually conforms the existence of these reactive intermediates species like carbenes. Even though they are in general short lived, but this type of carbenes are stable and can be detected through various spectroscopy methods.

In that particular topic we have discussed one specific type of carbenes that is called Arduengo carbene that that carbene if we now draw its basic structure ok; we I am in the last class I have shown its structure I am not going to draw the full ok.

So, now if we see this structure for this particular carbene and the next question come into our mind that why this is stable; why is it stable? So, there are few reasons behind this; number one is that the electron deficiency is in the carbenic carbon is reduced by the donation of the nitrogen lone pair. So, nitrogens are having lone pairs it can donate ok; so first one is that electron deficiency is reduced by the donation of nitrogen lone pair ok.

So, this nitrogen contains some lone pair; it can donate to this electron deficient carbenic carbon and in that way it can increase the stability. Number two the carbon carbene lone pair is stabilized by the inductive effect of these two electronegative nitrogen atom. So, these two electronegative nitrogen atoms are there; these two. So, they will have this inductive effect and due to this inductive effect, they will actually pull out this electrons from this carbenic carbon and that way it stabilizes this particular type of carbenes.

So, next one is that carbene lone pair is stabilized by the inductive effect of two electro negative nitrogen atoms ok. Next is that number 3; this type of bulky R groups that actually prevent the dimerizations. Though there are certain ah certain type of different type of these R groups are possible with very bulky to not that much bulky, but overall we can say that presumably the bulky groups prevent the dimerization ok.

So, turbines are in general dimerized because they are too reactive. So, in the presence of this type of bulky groups; they are not going towards the dimerizations. So, due to this particular reasons this type of carbenes are getting stabilized. Next we will learn another type of stable carbenes that is called phosphino carbene ok; they are also part of persistent carbene and that has been developed in 1988 by Bertrand group, this one by Professor Arduengo group ok. So, this is by Professor Arduengo Group ok.

Now in 1988 by Bertrand group; they also developed another type of persistent carbene that is called phosphino carbene. Now, how what is their structure? They are in general like this ok, this is a another way this these are called push pull carbene; push pull carbene. Why? Because of the contrasting electron affinities of the phosphorus and silicon; phosphorus and silicon atoms, due to that these are called push pull carbene.

Now how they can be getting stabilized? Because of this type of resonance ok; so these are called these phosphino carbenes. And in general they are called push pull carbene because of the contrasting electron affinities of the phosphorus and silicon atoms.

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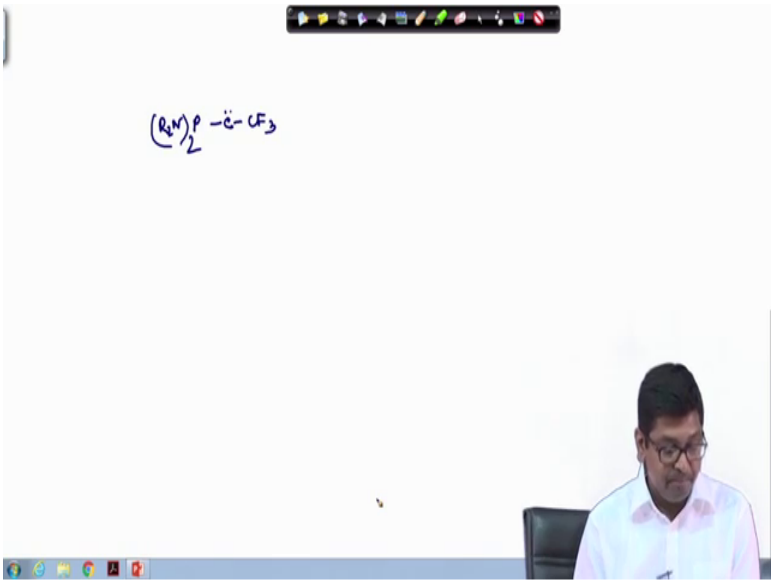

Another example of in this field is that and this type of carbenes they are also persistent carbene. In general it has been found that there are certain type of persistent carbenes are there which has been used as ancillary ligands in organometallic chemistry and in catalysis.

Especially these N heterocyclic carbenes they have enormous used in catalysis; especially in the asymmetric catalysis also it has enormous use because you can easily induce some of the chiral part in this molecules and they can take part in the asymmetric catalysis. So, these type of persistent carbenes they are very very useful not only in organometallic chemistry; again they are also very important in asymmetric catalysis ok.

Now we will learn another topic in this carbene that is the generation of carbenes.

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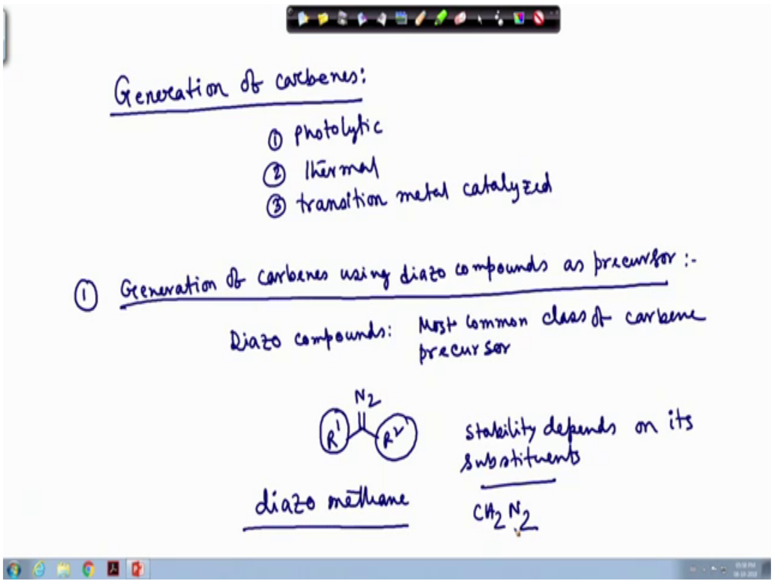

Generation of carbenes:

① photolytic
② thermal
③ transition metal catalyzed

① Generation of carbenes using diazo compounds as precursor :-

Diazo compounds: Most common class of carbene precursor

stability depends on its substituents

diazo methane

CH_2N_2

Whenever we are talking about carbene structure; its geometry, its stability then; obviously, we are always telling that they are in general very short lived and highly reactive. Except few persistent carbenes most of them are short lived and next questions will be that how we can generate, how we can form these carbenes; the short life species because we want to use them for various type of reactions. So, how we can control its generation in different reaction conditions? That we will learn.

In general it has been found that most commonly there are photolytic formation through photolytic cleavage of certain molecules, we can generate these carbenes. Number 2 is that thermal, number 3 is that transition metal catalyzed or we can say mediated in certain cases. So, using these three different techniques via the decomposition of the diazoalkanes or the suitable precursors we can generate carbene molecules ok.

What does it mean by decompositions of the diazoalkanes or suitable precursors? It means that loss of small stable molecules from these diazoalkanes or suitable precursors gives us the corresponding carbenes. So, now we will first see that generation of carbenes using diazo compounds as precursor. Why this is most common? Because very simple because if you see in this diazo compounds, there is a possibility to eliminate the very small stable molecule that is the nitrogen. So, once it can we can eliminate that from these ah these diazo compounds then we can easily generate our required carbene species ok.

So, diazo compounds a very important class of compounds ok; this is the most common class of carbene precursor ok; so this something like this fine. Now this type of diazo compounds its stability depends again on the substituents associated with it. So, its stability is depending on its stability depends on it on its substituents ok.

So, now what will be the simplest diazoalkanes? What will be? So, the simple diazoalkane is called diazo methane ok.

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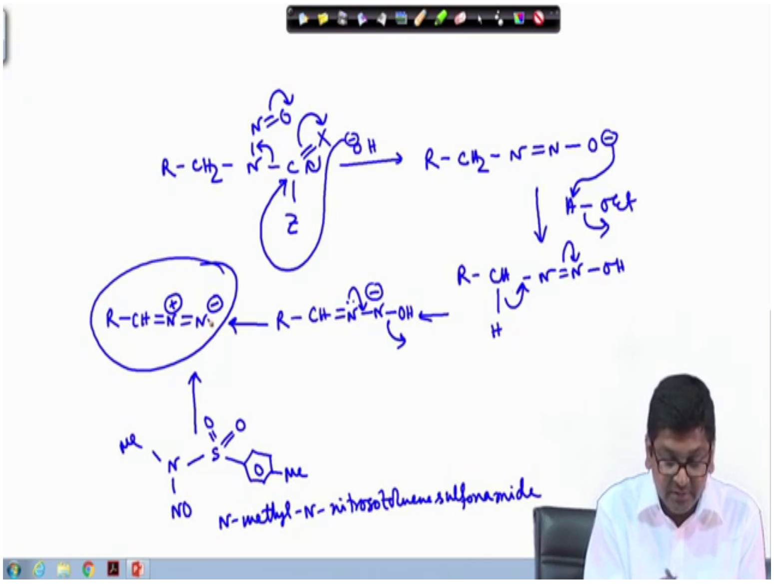

So, CH 2 N 2; in general diazomethane can be synthesized obviously, but this is highly unstable; this is highly unstable highly unstable it is toxic and explosive in nature ok; so it is very difficult to control it. So, during the synthesise synthesis of this particular diazomethane; it needs to be handled with a great care as it is as it is highly unstable toxic and explosive. So, it needs a proper care ok; in general it is used in solution usually in the diethyl ether ok.

Now, if we see its structure this is the diazomethane and stay like this sorry or it can be like this ok. So, if the diazomethane can be generated; then these can be a potential precursor for the carbene synthesis. Now first we have to know that how we can synthesise this diazomethanes? So, synthesis of diazomethanes; there are various method to synthesise diazomethanes I will utter few of them next is that synthesis of diazomethane fine.

In general the N nitroso derivatives of amides or sulfonamides in presence of base generates the diazomethane ok; so N nitroso derivatives of amides and sulfonamides. N nitroso derivative of amides or sulfonamides fine in sub base that gives this diazomethanes ok; how it can it can be generated; we will see the mechanism. Let us say we have this N nitroso derivative ok.

So, now we will attack over this electrophilic center; this will go this will come back then ok; so now fine once it will be like this. Now it is it has some protic solvent it will pick up; so now this one once it has picked up this now this will have this hydrogen ok. Now, so and once it is like this then the elimination of this OH minus again will give ok; so in this way we can generate this diazomethane.

Now, in similar fashion; this can be again synthesized from N methyl nitroso N nitroso para toluene sulfonamide. You can try its mechanism by your own it will be almost similar way that it can proceed and generates the diazomethane in presence of base ok. So, this is N methyl; N nitroso toluene sulfonamide. So, this is the N methyl; N nitroso toluene sulfonamide ok, from here also you can easily generate these diazomethanes fine. So, now we know how to generate the diazomethanes.

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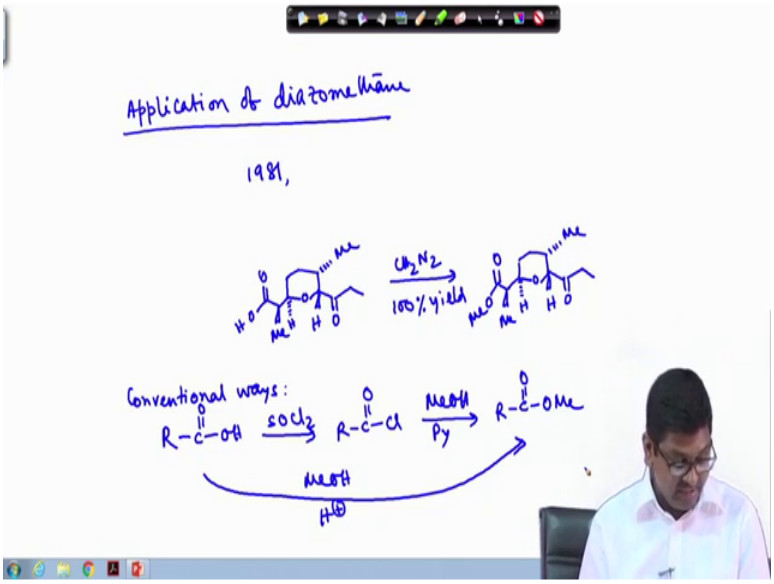

Application of diazomethane

1981,

Conventional ways:

$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Py]{MeOH} R-\overset{O}{\overset{\|}{C}}-OMe$$

Now, some applications of this diazomethanes we will learn ok. In 1981, some chemists in Pennsylvania; they were working on the synthesis of some antibiotic. During that synthesis some certain part of that molecule there was some carboxylic acid groups; so, they wanted to make its methyl ester. Now they had used this particular technique or method to make this carboxylic acids into its methyl ester in one step and the yield is almost quantitative ok.

Let us see what they have done during that time. So, this is a highly substituted tetra hydropyran ring; so what they had done ok. So, in presence of diazomethane; the yield is almost quantitative. So, it was converted into its methyl ester ok; in general how we can make one carboxylic acid into its methyl ester? If we see the conventional way; so generally if we are using carboxylic acid they are making its acid chloride ok. Then the corresponding alcohol in presence of base will generate this acid chloride into its methyl ester or else they can use this one with the methanol in presence of acid.

But these methods are having its own limitations and it cannot be used for all certain type of molecules; there will be lot problems in many reactions; so we need alternative. Here they have use diazomethane to convert carboxylic acids into its methyl ester as an very efficient alternative of those conventional methods of making carboxylic acids to its methyl ester.

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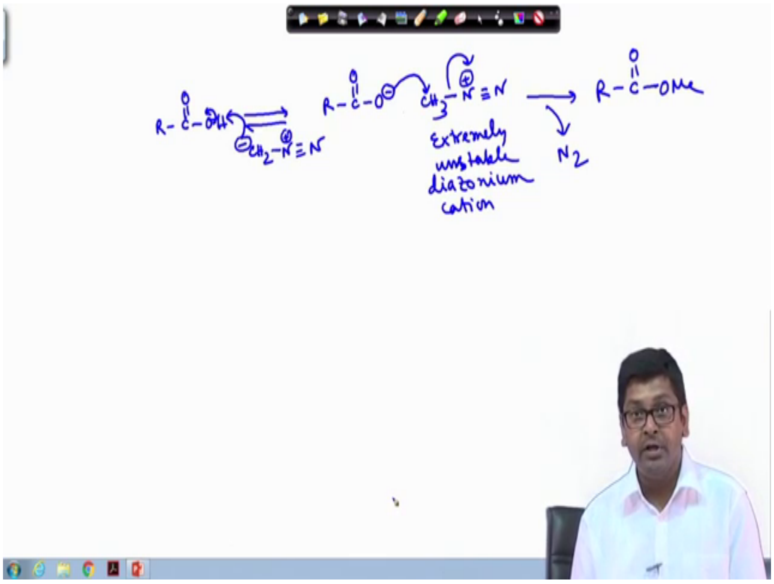

Now, we will see that what is its mechanism? If we see the mechanism let us draw the carbolic acid; now there is the diazomethane this carbolic acids this hydrogen is pretty acidic. Now this will pick up this hydrogen and ok. So, it will be plus CH 3 ok.

Now this is very good substrate for getting substitution by the suitable nucleophile; now it these are generated these two species I will not give like this way rather we will say that these two species has been generated from this reaction. Now this can nicely attacking sn two fashion to this extremely unstable diazonium cation; it will attack and nitrogen is very good leaving group; so it will eliminate nitrogen. So, it can nicely generate the methyl ester ok. So, the carbolic acid in presence of diazomethane it can nicely generate the methyl ester of this corresponding carboxylic acids.

Thank you very much for your kind attention.