Reactive Intermediates: Carbene and Nitrene

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Lecture - 01
Introduction

Hello everybody welcome to my course Reactive Intermediates Carbenes and Nitrenes. I am Dr. Rajarshi Samantha from Department of Chemistry IIT, Kharagpur. Before going into the detail of this course I would like to introduce that what is this reactive intermediates. Now, if we see all organic transformations or rather I should say most of the organic transformations are going via multiple steps that means, they do not proceed in a single step.

Now, in the several steps are required to get the desired product from a organic reactions. During this multistep reaction sequences, there are lot of short lived species can be generated, which quickly convert into different products, side products, other intermediates different reactants etcetera. They are in general very short lived species highly reactive and the way they are very seldom isolated, these are actually called that reactive intermediates.

Now, why they are important, because all these reactions are generating these particular short lived highly reactive species. So, that is why it is very important to understand those reactive intermediates, how they are forming, what are their roles in the reactions and how their structures are actually getting shaped etcetera. Now, as they are very short lived it is not easy to determine their structures, but there are several experimental and theoretical calculations are there that can predict or determine the structures and geometry of those particular reactive intermediates.

Now, there are different reactive intermediates generated during the organic transformations.

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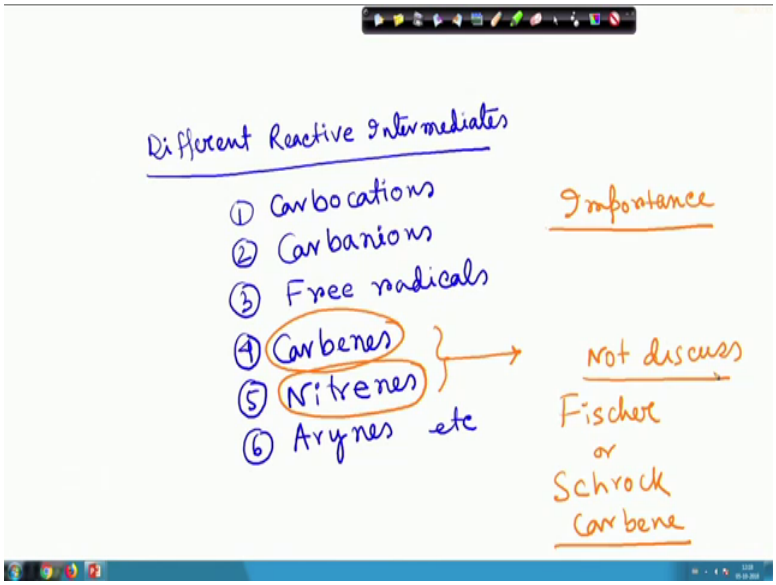

As per example, as per example carbocations, carbanions free radicals, then carbenes, nitrenes, arynes etcetera. So, among all these reactive intermediates in this particular course, we are actually interested in these two reactive intermediates, that is one is carbene another one is nitrenes. Now, question is that why we would like to learn them what is their importance. If we see in various synthesis of drug molecules bioactive natural products, pharmaceuticals or organic materials of importance are actually during their synthesis, they are actually taking help of this particular intermediates.

That means for the synthesis of such type of biologically important compounds, the reactions required there those reactive intermediates are forming. So, I will show you in the later of later part of this course that, how these reactive intermediates like carbenes and nitrenes are important in the transformations of various organic molecules and, how they are taking part or how they are actually emphasizing that reaction that we will learn. Now, the thing is that in this particular course, we will not discuss the Fischer or Schrock carbenes, we will not discuss in this particular course. That means, this metalocarbenes we will not cover in this course.

Now, what are the books that we will follow this for this particular course like the books are Advanced Organic Chemistry Part B by Professor F A Carey and R J Sundberg, then next book is Organic Chemistry by Professor J Clayden, N Greeves and S Warren. Next is Carbene Chemistry by Professor W Kirmse finally, the Reactive Intermediates in

Organic Chemistry by Professor Maya Shankar Singh. So, these particular four books we will follow for this topic.

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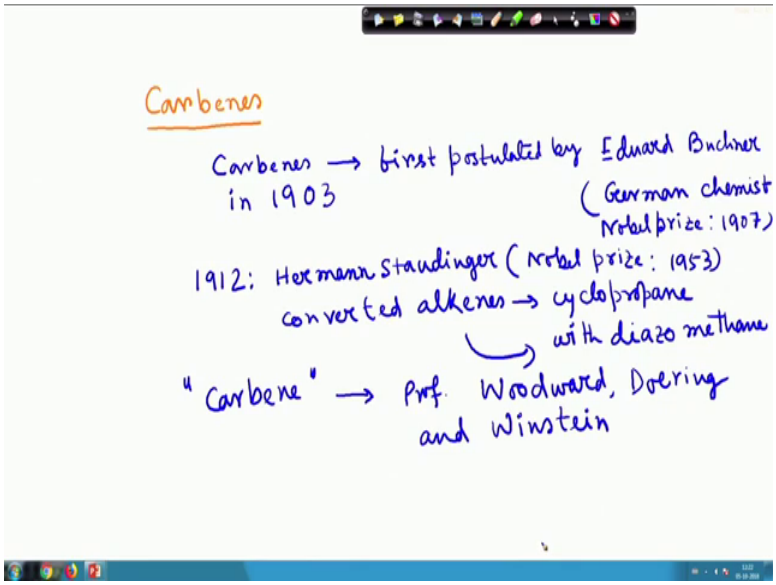

Now, we will discuss about the carbenes. Carbenes were first postulated by Professor Edward Buchner, carbenes first postulated by here I would like to mention that he is a German chemist and got Nobel Prize in 1907. However, Professor Edward Buchner first postulated these carbenes in 1903, then in 1912 Professor Hermann Staudinger, who also got Nobel Prize in chemistry in 1953 he also converted alkenes into cyclopropane, with diazo methane with the help of diazo methane.

That means that these carbenes was previously known and people have slowly developed this chemistry. Finally, this term carbene actually conceived by Professor Woodward Doering and Winstein, even though this species was known before, but the name of this carbene that actually conceived by Professor Woodward Doering and Winstein.

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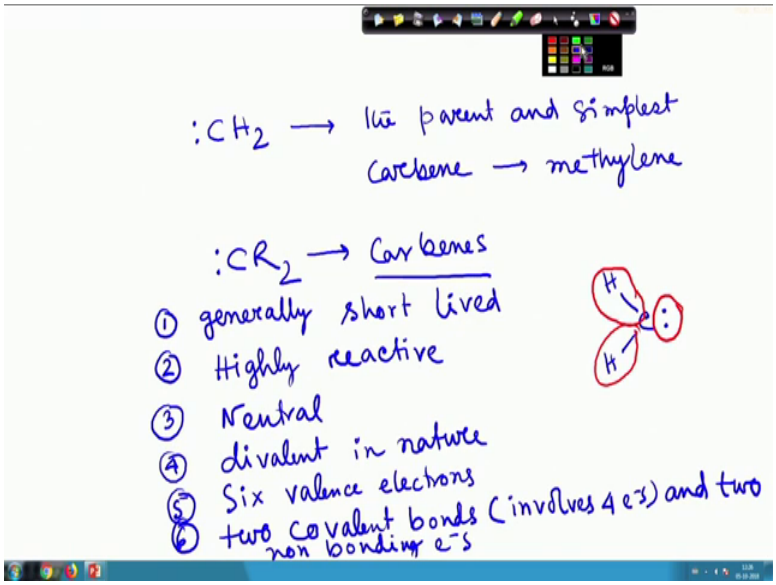

Now among all these the parent carbene molecule is actually this one, this is the parent and simplest carbine, its actual name is methylene, but now for all these substituted this type of species are actually called carbenes ok.

Now, what are their characteristics? Their characteristics are as I mentioned before like all other reactive intermediates, their characteristics are number 1, definitely they are in generally short lived; that means, lifetime of those species are very short, definitely they are highly reactive ok. Next the fundamental difference between this particular reactive intermediates with the other reactive intermediates are here, they are neutral; that means, their formal charge is 0, they are unlike other reactive intermediates they are divalent in nature ok. They have six valence electrons ok.

Among them among these six valence electrons, they are actually having two covalent bonds that involves 4 electrons and two non bonding electrons ok. So, these are in general their characteristics like, they are short lived highly reactive, neutral, they are divalent in nature, they contains six valence electrons and they have two covalent bonds and two non bonding electrons. That means, if you have this they have these two covalent bonds and these two non bonding electrons; that means, they are having these two covalent bonds and these two non bonding electrons ok.

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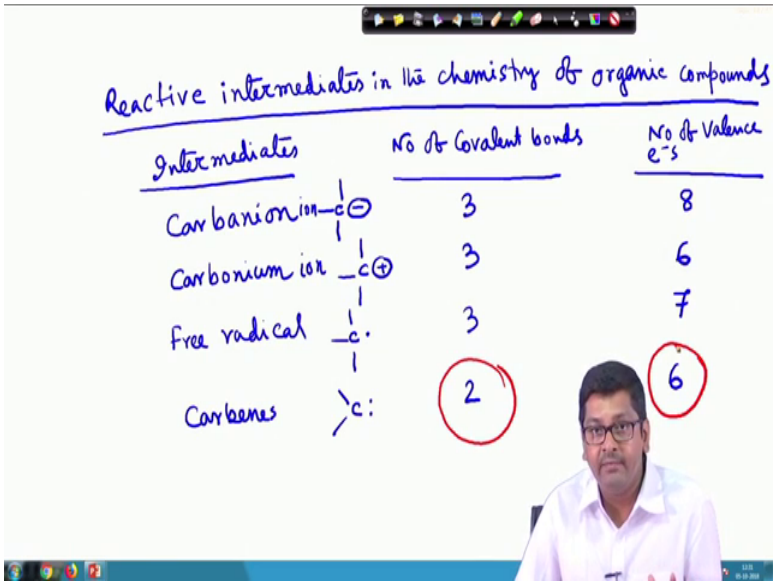

Now, if you see all these reactive intermediates, how they are differ in nature with the carbenes. So, reactive intermediates in the chemistry of organic compounds ok. So, first we will write the intermediates ok, then number of covalent bonds ok, then number of valence electrons fine first consider carbonion. So, this is having the number of covalent bonds ok. So, number of covalent bonds is 3 number of valence electrons definitely 8, next is the cabonium ion ok.

So, fine so, in case of carbonium ion again number of covalent bonds is 3, but unlike the carbonium carbon ion ion here the number of valence electrons is 6 then the free radicals select this. So, here also number of covalent bonds are 3, but number of valence electrons is 7. Next if we consider our interest that is carbenes there so, here number of covalent bonds unlike other reactive intermediates here it is only two and number of valence electrons also here it is 6 ok.

So, these are the reactive intermediates in the chemistry of organic compounds, where if we consider the those important intermediates, where carbon ions ion that contains number of covalent bonds 3 number of valence electrons 8, carbonium ions number of covalent bonds are 3, number of valence electrons 6, free radicals again here number of covalent bonds 3, number of valence electrons is 7 and for carbenes number of covalent bonds are 2 and the number of valence electrons are 6 ok. So, these are the basic differences between all those reactive intermediates I mentioned. Here the important

thing that I want to mention again that here, if you see that number of covalent bonds that is having 2 and number of valence electrons that is 6. This shows that these types of species are highly electron deficient in nature.

So, they will be must be highly reactive; that means, they are very much eager to get another two electrons to fill up their octet. So, they will be definitely highly reactive ok.

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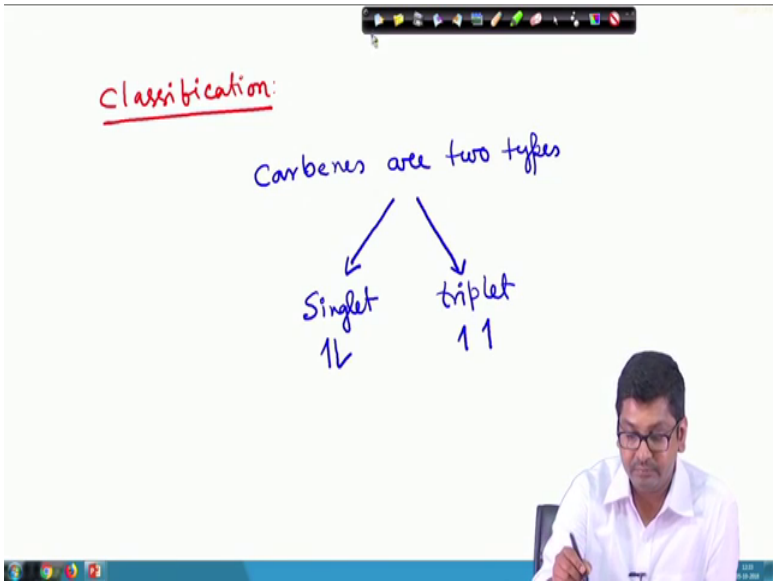

Next we will discuss the classification of this carbenes ok. So, carbenes are two types one is called singlet and another is called triplet. Now what is their difference? They differ in the electronic structure, triplet means it should be like this type and singlet means it should be like this.

Now, how they behave or what is their geometry, what will be their structures that we will discuss in detail. Now, question is that these carbenes when that generates, whether that will be singlet or triplet that can be again guided by the reaction conditions ok. So, now we will see that these carbenes that is singlet or triplet, how they will behave in the reactions definitely, they will behave differently right. So, singlet carbenes will behave differently and triplet carbenes also behave differently. Now, we will learn the structure and geometry of the carbenes ok.

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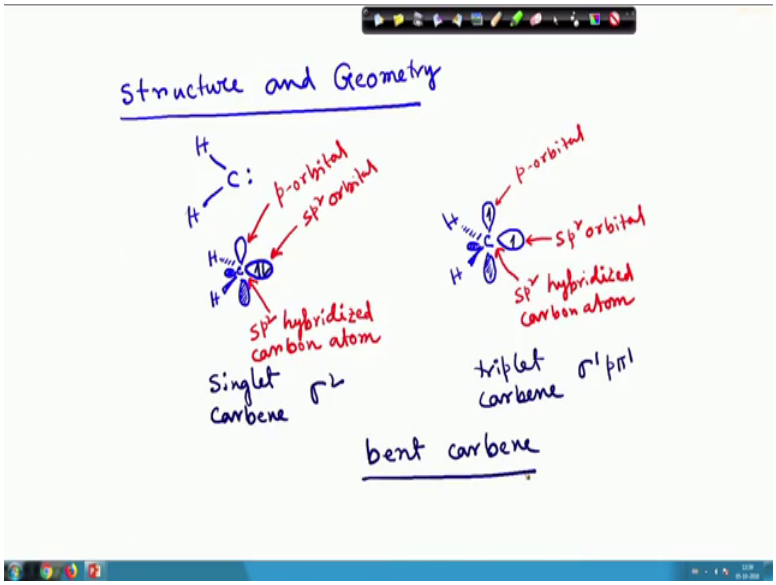

So, our the next topic that will be discussed that is the structure and geometry of the carbenes. First we will see this is the carbenes, now we will draw its structure and geometry ok. So, this is the sp 2 hybridized carbon atom ok. And this is the p orbital ok, and this is the sp 2 orbital ok.

Now, if we take the electrons, now that can stay like this. So, this is called what I previously mentioned that singlet carbene ok; that means, two electrons that is in this particular sp 2 orbitals and they are paired up ok. Next the same thing they can stay like this way ok. So, they can stay like so, this is the again like earlier this is the p orbital, this is the sp 2 orbital this one also sp 2 hybridized carbon atom ok. So, now, this is the sorry.

So, this is the triplet carbine, actually here you can write it like a sigma 2, this and here it is we can write like a sigma 1 p by 1. Because this is in p orbital 1 electron and 1 electron is in this non bonding orbital sp 2 orbital ok. In general these are actually bent in structure bent carbene ok. So, their structures are bent.

Thank you.