NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

IIT BOMBAY

CDEEP
IIT BOMBAY

Organometallic Chemistry-I

Prof. Debabrata Maiti
Department of Chemistry, IIT Bombay

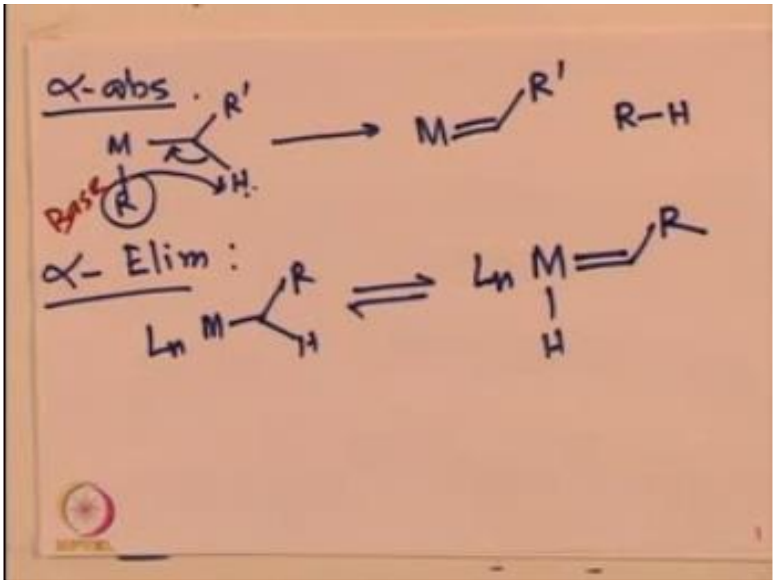
Module No. 3

Lecture No. 13

α - ABSTRACTION & B – ABSTRACTION

Welcome everyone today we will continue discussing on α abstraction and β abstraction we have seen α elimination and β elimination and corresponding the reverse reaction. Today we will mainly focus on α abstraction and beta abstraction. As you know the products which we are going to get by this transformation are going to be exactly same to that of α elimination and bait elimination. But still there are fundamental differences that can that can distinguish these processes let us try to look at these in greater detail.

(Refer Slide Time: 01:02)



So the α abstraction, α abstraction is mainly a process where you have your arm your metal alkyl species and this in this particular case you are going to get these α position hydride of abstraction directly by something else it reaches let us say attached with the metal center, here there is no association of metal hydride at such there is no metal hydride intermediate bond formation.

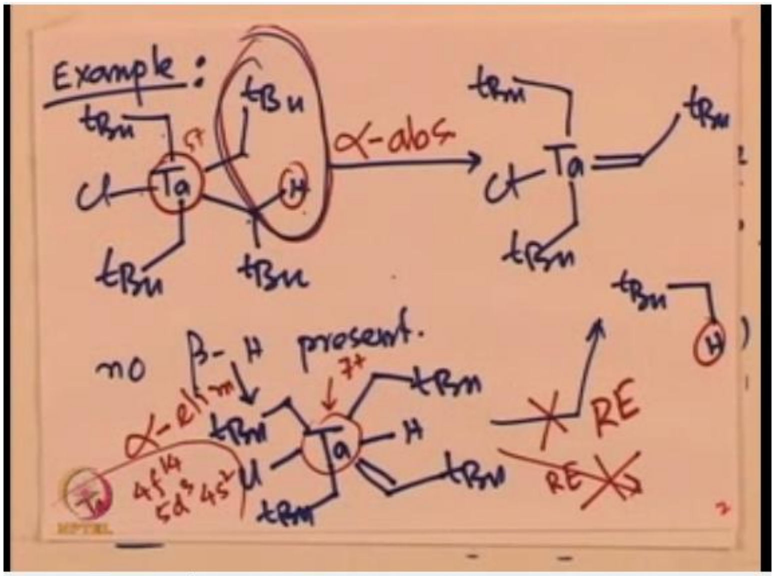
This is the α abstraction net result is giving you metal carbon species if you just compare want to compare the α elimination this is very simply let us say you have a ligand metal complex and an alkyl intermediate of course these reactions are reversible in nature, and at the end you end up getting ligand metal hydride species along with these carbine intermediate. So if you compare these two reactions the first one versus the second one of course the product wise it looks similar right, both of them forming a carbine intermediate.

But in this case there is no metal hydride bond formation over here in α elimination as you have seen there are, there is this metal hydride bond formation. In this particular case this one this alkyl group is acting as a base okay. So this is the base over there and this is the reaction first done by stock okay experimentally proven by stock will in a moment we will see the see the difference or see the more exotic example of this category.

So what we have seen right now the α abstraction and α elimination are similar, both of them are giving the exactly same compound so to speak the carbine compound, but mechanistically they are different there is a very subtle difference between these two in the α abstraction case the metal alkyl intermediate, the alkyl can be the base itself and can abstract the hydride α hydride directly without passing through a metal hydride intermediate.

Whereas for α elimination we have seen there is inevitable formation of metal hydride intermediate. But once again both of them are forming or giving the exactly same compound that is the metal carbine intermediate. Let us try to take an example we have previously seen the many examples of α elimination. Now let us try to look at closely one of the real-life example of these α abstraction reaction. So this is an example by stock and we will discuss briefly about it, it is a tantalum complex let us try to look at these complex.

(Refer Slide Time: 04:01)



Now we have this tantalum at the center and we do see one alkyl group two alkyl group three and four most interestingly you see there are at every α carbon center there is a hydrogen atom available but at the β center there is no CH bond available of course it is a highly engineered molecule it is an organometallic intermediate which is kind of designed or by default it came out to be the one which will not have any β hydrogen so only hydrogen only hydride present over there is the α hydride okay.

Now if you try to look at it very carefully the product we are going to get from this reaction is going to be a it is going to be a are being intermediate where this tantalum intermediate undergo for the reaction to give you the product okay so what we have seen in over here is very simply this whole moiety is undergoing obstruction and giving you the carbon moiety so of course the other product in this case you are going to get is this one right and this hydride is going to be the one over here.

Of course you know most important thing once again is no β hydrogen present right that is no surprise on the other hand there could be another alternative mechanism that is α elimination before drawing that let us try to look at one more time carefully there is only α hydrogen present no β hydrogen present at any of the of this alkyl group here one of the alkyl group is acting at the base abstracting the hydride from another alkyl group and this is the α hydride and we are getting this carbine intermediate alternate mechanism involve the formation of as you can see you can one can imagine it can form these tantalum hydride and this tri butyl intermediate right.

So everything else remains same from a one two three four five member intermediate we can technically get a seven-member intermediate right so the seven-member intermediate okay if you try to look at this we are calling as α abstraction this should be α elimination so these are thus these are both of them are leading to the same product of course next step would be as you can imagine reductive elimination from here should give us the same product so what we have seen.

So far in this example particular example is a is a tantalum complex no Penta coordinated complex having four different alkyl group without any β CH bond we have only α CH bond it can give us α abstraction where one of the alkyl group can act as base to give metal carbine intermediate on the other hand and α elimination mechanism can follow where a metal hydride species is because forming in the process we are getting the carbine intermediate and then alkyl and hydride deductively eliminate to give you the same product as we are getting from α instruction.

Now the query is the very simple question one should ask which one should favor which one is likely in this let us say particular case of course most of the cases you see the α reaction α abstraction or elimination type of scenario most of the scenario we are going to get α elimination reaction but there are special cases of course this is one such case where I think α we will see in a moment α abstraction is likely.

But α elimination is not going to happen and why is that very simply if you try to look at that example one more time, let us try to go back and try to look at the example one more time this is the one where we have one two three four five six seven, so this tantalum is going to be tantalum 7+ now if you do the outer electron configuration for the tantalum you would know this is going to be $4f^{14}$ okay $5d^3$ and $4S^2$ right.

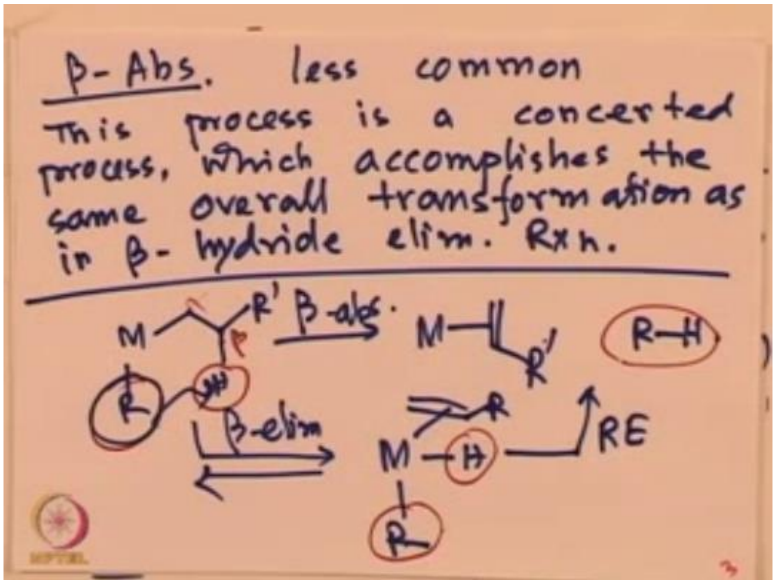
If this is the outer electron configuration now you can see only five electrons that means over here 5+ is likely 7+ for tantalum is a bad extremely bad process, so it is not going to happen so you can say that reductive elimination should not should not be happening so this process should not be happening and therefore this product formation can only be justified the product formation what we see in this particular case can only be justified by α abstraction.

α elimination although one can draw it but it is electronically not going to be favorable because it required a tantalum 7+ which is not feasible and it and it is unlikely and therefore the α elimination and following reductive elimination subsequent reductive elimination will not be a feasible idea it is all the way are going to be α obstruction that is direct obstruction direct mechanism.

No such metal hydride formation will be happening all right, next of course we would like to discuss a little bit more on this topic and that is that is the β obstruction which is quite related, so but now we are going to see is how β elimination and β obstruction differs, you have seen that difference between α obstruction and α elimination now we are going to see β obstruction and β elimination.

Once again both of them will give exactly same product but mechanistically or you know in terms of electronic properties of the metal complex electronic properties of the metal complex it will be different let us try to look at the β abstraction layer.

(Refer Slide Time: 11:10)



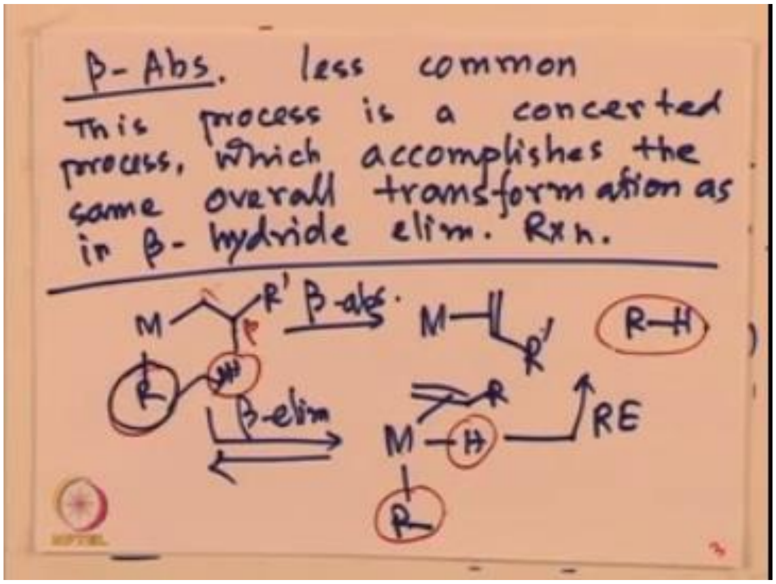
β- Abs. less common

This process is a concerted process, which accomplishes the same overall transformation as in β- hydride elim. Rxn.

So β abstraction now of course this is less common way common intermediate or more common pathway and you have learned is the β elimination, so this is a this process basically is a concerted process of course again just like your α obstruction it is a constant it is a concerted process which accomplishes the same overall transformation that is what is most important to remember. This gives you exactly same transformation overall as in β hydride elimination, okay.

So what we try to tell you is it is exactly the same process okay, a bigger abstraction is similar process compared to your that beta elimination but mechanistically they are going to be different and sure you have remembered the elimination process we have discussed quite a lot about it and with a lot of example over there. Now we will bring your you know main transformation one more time just to compare and contrast that beta elimination with beta abstraction okay.

(Refer Slide Time: 12:53)



β- Abs. less common

This process is a concerted process, which accomplishes the same overall transformation as in β- hydride elim. Rxn.

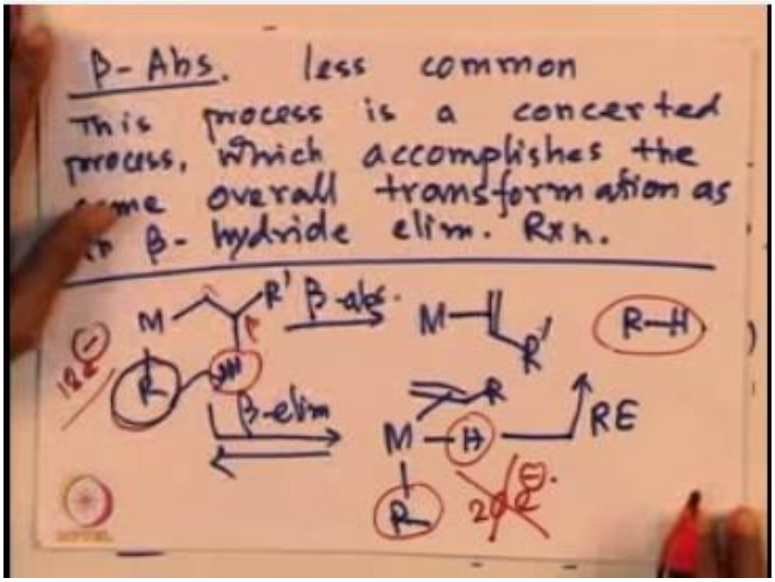
Let us first try to look at the beat abstraction reaction, so what we are going to get in this case of beta abstraction simply is this is acting as a base so it will directly abstract the beta hydrogen and overall we are going to get let us say this intermediate and RH. If this one was undergoing let us say beta elimination then we will get metal hydride intermediate along with let us say R and then olefin intermediate formation subsequent reductive elimination should give you this intermediate.

So as you see it is exactly similar for beta abstraction you do not have any metal hydride intermediate involved it is direct the base alkyl group one of the alkyl group or one of the moiety on the metal center directly abstracting the hydride from the beta position, alpha beta, beta position and giving you RH in the process these R and this H without any metal hydride bond formation.

Whereas in case of beta elimination it is going to be metal hydride along with the metal alkyl intermediate present and then these two intermediate these two species will undergo reductive elimination to give you the same product. So essentially what is important to understand is you know this is exactly the same process as you see the net outcome is the is the alkaline formation along with the metal olefinic intermediate formation so both the beta hydride elimination and beta abstraction is exactly giving the same compound.

Now one must remember these process differs very little but then there are situation where only for example beta abstraction is favorable one second beat elimination is the most preferred pathway and most often let us say 99% cases or 95% cases you are going to get the bigger elimination but then there of situation where beta abstraction is the only pathway because beta elimination can be rule out or is unlikely to be happening, okay.

(Refer Slide Time: 15:28)



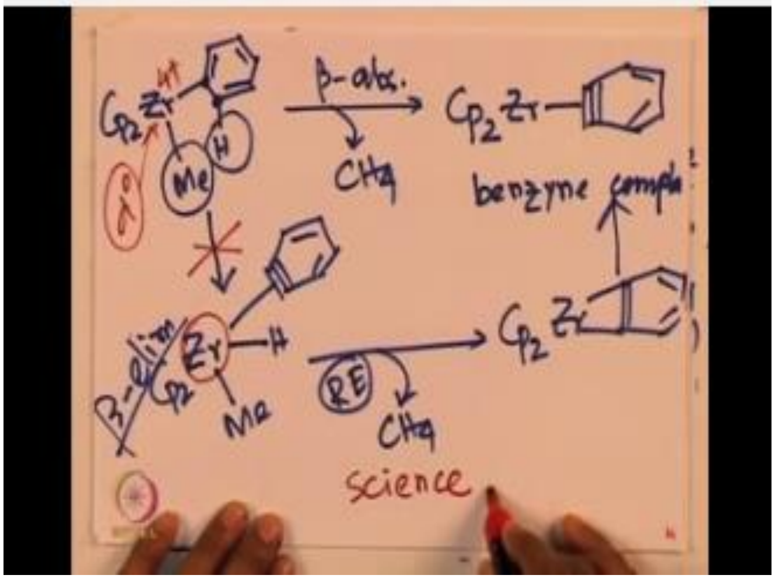
β- Abs. less common

This process is a concerted process, which accomplishes the me overall transformation as β- hydride elim. Rxn.

So for example if you look at if this intermediate is18 electron species now this for this to happen is 20 electron species right, so these perhaps will not happen if you are starting with an 18 electron species like this and then this is not going to happen therefore if you are getting this product this is likely that you are going to get through or go through a beta abstraction intermediate, okay. Now of course to prove which one is likely or which one is happening.

Particularly way that it is an elimination versus obstruction it is not an easy experiment to do it requires extremely good extremely efficient synthetic design it requires beautiful design of the organ metallic intermediate so that β abstraction is the only preferred pathway and β elimination is disfavored completely there are very few examples that exists of this category but the first one we will discuss which is a classic in its own right. This is a jerk gonium complex.

(Refer Slide Time: 16:42)



And CP to zirconium complex along with the methyl group okay now you see this is α hydrogen is not present this is the β hydrogen so β hydrogen inflated of course the product you are going to get let us say by β abstraction as you can imagine the product formation you can go about these two group and ch4 can go out and therefore what you have in CP 2 zirconium and this banjo in intermediate right so this is benzyme complex this is benzyme complex.

Now most importantly 11 could think of course that this zirconium should give you this intermediate okay and where this benzene can coordinate with this overall to give you finally from their own we can give get the reductive elimination in the form of methane so this is going to be your first step and then subsequently with an elimination overall you should get a CP to zirconium and this intermediate which should then give you then give you the final product which is nothing but digital products are exactly same.

Now if you look at their this is the one we are talking about is β elimination reaction okay this is the one which is the β elimination reaction now if you look at this process okay both we have seen β obstruction and β elimination the first one the first error we were trying to draw is the β abstraction where direct method formation was going on there is no metal hydride intermediate involved in this case the other pathway we have big elimination where we have seen the metal hydride intermediate is forming and subsequently a reductive elimination is happening to give you the exactly same compound.

Now the major query in this case the major thing one should look at for this case is β elimination likely if β elimination is not likely to happen and the product formation is still there therefore there is only one way to explain this observation and that is β abstraction okay let us try to go back one more time in with this with this example where we do see that this zirconium now if you look at this zirconium is a d0 Center a zirconium 4+ zirconium is 4+ that is d0 center now as you know this for this metal hydride formation you should have the D electron available to undergo such intermediate right.

So this is this process is not likely to be happening, at the centre when you have a d_0 metal present since it is a d_0,present d_0 metal centre having a metal hydride bond formation, is not going to be feasible and therefore what we can say, in this case particular case this is a classic example, of these beta abstraction reaction not beta elimination, it is a d_0 metal centre there for further metal hydride intermediate formation is not going to happen, and therefore we are going to get only beta abstraction, which is a paper which is classic in its own right.

This is a science paper by Steve buck wads group in 1993 261 1696 okay, so in this class what we have seen so far is, it's very subtle difference between alpha instruction and alpha elimination, similarly very subtle difference between be the instruction and beta elimination, of course these examples are highly engineered example, not in every case you will see alpha obstruction or beta obstruction, only in rare cases but that is that is most important to remember and understand, and therefore knowing that beta obstruction and alpha obstructions are possible, is one of the most important thing in this in this field, that although alpha elimination and beta elimination is likely or more often happen.

But alpha obstruction and beta obstruction one should not and must not rule out, therefore one must be extremely careful before commenting, on whether this is an instruction for elimination one must count the electron, and just the scenario and therefore they must proceed with the formation of the product by a particular mechanism, of course it's always very difficult to prove a mechanism.

But if we know the fundamentals of different pathways I think we can have some educated guess, about the mechanism I'll support it with some experimental evidences, okay in the next class will be mainly discussing the force entered reaction mechanism, so we have seen show for different pathways for product formation, there are different few other pathways for fundamental pathways, for product formation in the next class we will see for centre reaction mechanism, or so called Sigma bond metathesis.

We will also see 2+2 the accents, okay so call those are very famous Nobel prize-winning reactions, so we will see both Sigma bond metathesis and two plus two reactions in the next class, well till then you all of you keep reading and keep make sure that you understand the subtle difference between these processes, these are fundamentals of oregano metallic chemistry and one should have a strong grasp, of these principles before they want to write down any mechanism.

And very simply once one can digest one can feel this mechanism, very efficiently writing organometallic intermediate is our organometallic mechanism, is not a big deal at all what one should, the but therefore one should not really you know really take it easy on the fundamental understanding. This should be one should be very careful and very simple in understanding what is going on, with that for the next class we will discuss the four central mechanism's well as your two plus two reactions okay, till then see you later bye.

NPTEL
Principal Investigator
IIT Bombay

Prof. R.K Shevgaonkar

Head CDEEP
Prof. V.M Gadre

Producer
Arun Kalwankar

Digital Video Cameraman
&Graphics Designer
Amin B Shaikh

Online Editor
&Digital Video Editor
Tushar Deshpande

Jr. Technical Assistant
Vijay Kedare

Teaching Assistants
Arijit Roy
G Kamalakshi

Sr. Web Designer

Bharati Sakpal

Research Assistant
Riya Surange

Sr. Web Designer
Bharati M. Sarang

Web Designer
Nisha Thakur

Project Attendant
Ravi Paswan
Vinayak Raut

NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)