Transition Metal Organometallics in Catalysis and Biology
Prof Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology - Bombay

Module No # 05
Lecture No # 31
Alkene Alkyne Metathesis (Part – 3)

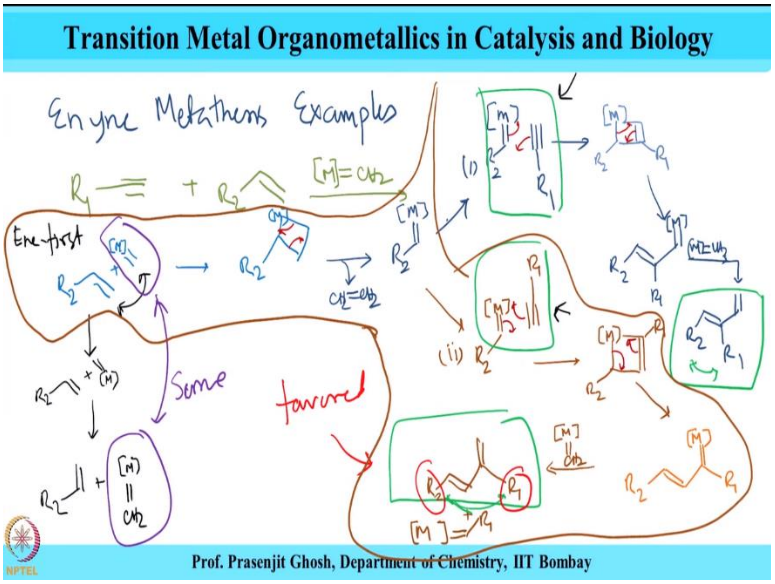
Welcome to this course on transition metal organometallics in catalysis and biology. We have been discussing alkene alkyne metathesis in the past few lectures. In particular we have looked at various types of alkene alkyne metathesis reaction which are known. We are also looked at the mechanism possible pathways that are that have been proposed for this alkene alkyne alkene alkyne metathesis mechanism.

What we are noted is the fact that this alkene alkyne metathesis mechanism reactions are usually done under high dilution conditions where these alkene alkyne metathesis are eneyne metathesis are performed on substrates containing double bond and triple bond in a intramolecular fashion were by minimizing the secondary reactions like cross alkene and cross alkyne metathesis reactions.

We have also seen that in this alkene alkyne metathesis reactions or eneyne reactions the most popular view is of the fact that these eneyne metathesis reaction proceeds with alkene getting admitted metathesis first followed by alkyne which leads to singular or more reduced collective products. Whereas if the possibility for the other mechanism which is alkyne first mechanism would lead to various (()) (01:55) isomers which have also been explained.

And we had also seen in the previous lecture that utility of utilizing ethylene C_2H_4 in carrying out this enyne metathesis reaction helps in increasing the catalyst active species concentration and also reducing their resting state time. So with that we move into today’s lecture where we are going to take a look at some of the examples of this alkene alkyne metathesis reaction.

(Refer Slide Time 02:30)



Transition Metal Organometallics in Catalysis and Biology

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

And now the reaction is given for the substrates which is the carbon catalyst now that the possibility of this reaction happening can give rise to two types of products which we are going to sort of disclose as we say so proceeding along the first ene first strategy so that would imply this reacting with CH2 would give R metallacyclobutane intermediate like the one shown would give the corresponding carbene active species plus ethylene.

Now these then could react with acetylene maybe in first scenario it would be this is R2 and R1 would give the species R1 and then subsequent rearrangement would give R2 double bond this R1 this product. Whereas the other possibility which is the possibility 2 of R2 this reacting this R1 and this confirmation would give the corresponding species that would again undergo rearrangement the way it is shown R2 R1 maybe the way it is shown to it with the proper color of the ink R2 R1 this reacting with again the CHR2 would give +R1.

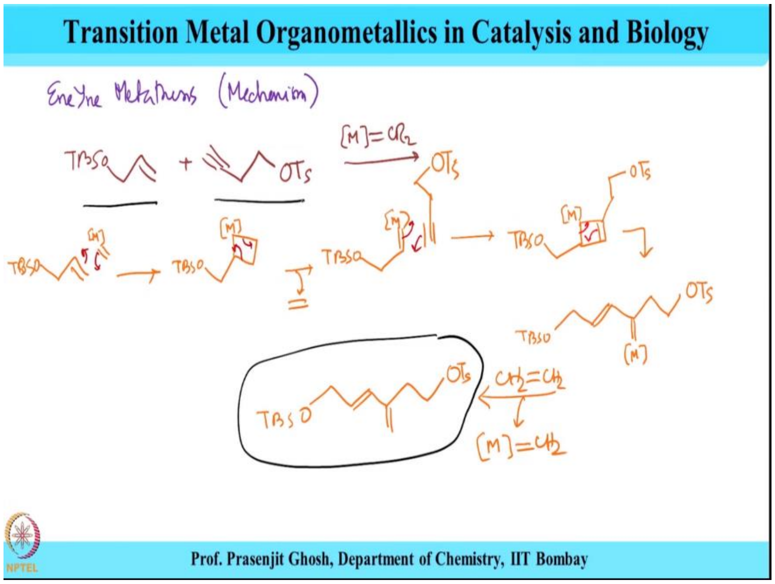
And similarly in the parent case these reacting with would give R2 R1 this. So what we what can be seen that there is a possibility of 2 kinds of products coming out of it the 1 which is shown over here. Where this R1 and R2 is in (()) (10:43) conformation to each other and the other possibility is this where this R1 and R2 are away from each other. So these are the 2 possibilities which emerge and these arises primarily due to the 2 different orientation of this active catalyst reacting with the alkyne as it is shown over here.

This leads to 2 different products of these the one which is favored is this favored and mainly because of sterics reasons where this R1 and R2 spread far apart. Now in this mechanism what I had done I had just carried out the ene first this is the ene first mechanism that means the first is metathesis between the alkene and the active species and then the mechanism is between the active species and the alkyne so in the ene first mechanism the pathway that I have shown is of 1 type there exist another orientation as well which I will draw it right now.

And these will thus give the product which is shown over here. So the point to note that these pathway does not go any further because these active species and the starting active species are the same. And this kind of orientation does not lead to the product. So to sum up in this in first strategy the reaction proceeds by the mechanism which is shown over here. And I am going to separate this in the 2 pathway I am going to separate this as the 1 in the brown which is what is the favored product.

So this is how the reaction proceeds and there are other possibilities are also outlined. And so this was a nice demonstration of the ene first mechanism that we had spoken and we are going to take a look at some more examples during the course of this talk. Where we are going to see some other examples where such eneyne mechanism indeed occur.

(Refer Slide Time 14:27)

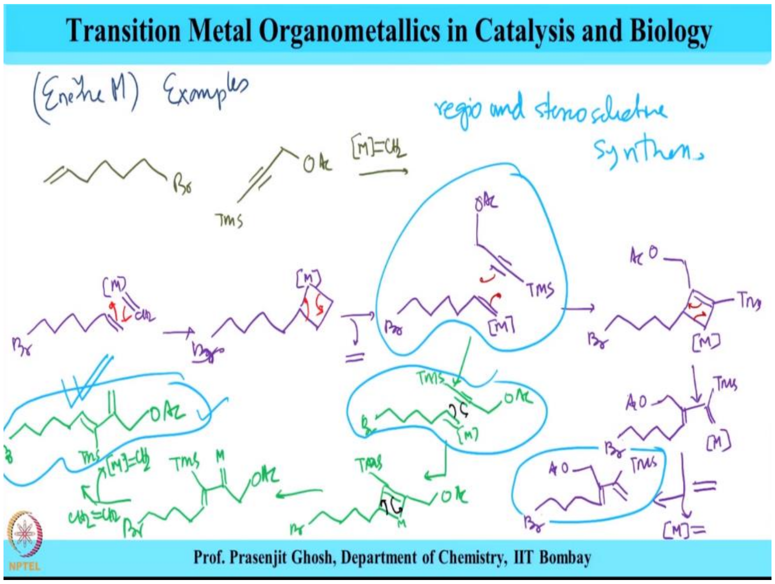

Transition Metal Organometallics in Catalysis and Biology

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

So similarly so in this case as well the reaction is between TBSO this alkene OTs in presence of metal carbene catalyst and this can also be worked out as is shown here. So this will start with the olefin reacting with this giving metallacyclobutane that will undergo rearrangement as shown to give. And a olefin which is nothing but ethylene now this would react with the alkyne substrate OTs in the way it is shown here to give TBSO OTs that would undergo giving TBSO OTs.

And then this reacting with CR2 CH2 would give the olefin that would on reaction with ethylene would give and the desired product as it shown. So this is the product which is formed from the reaction of TBSO vinyl olefin with the acetylene as is shown over here.

(Refer Slide Time 20:37)



Transition Metal Organometallics in Catalysis and Biology

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Some more examples along the similar fashion would be seen in this slide eneyne metathesis examples and this is between the reaction between bromide TMS or acetate or with a metal carbene complex as the catalyst. And this can be worked out in a similar fashion as it is shown. This orbit would go through this intermediate to give a metallo bromo cyclobutane intermediate.

That then would undergo rearrangement to give the ethylene as the side product and as the active species which would then undergo the reaction with TMS OAC. And also undergo rearrangement as is the way shown over here OAC. So this would undergo rearrangement as it is shown and this would mean that be a OAC TMS and this reaction with olefin would give back and TMS OAC.

Now there is another possibility that also exist in this case which is shown over here. This reacting with TMS OAC and that would also undergo rearrangement as it shown here would give intermediate like this TMS and this would subsequently give the product TMS OAC and that upon reaction with C2H2 would eliminate metal carbene to give the product TMS. So what we saw is that depending upon the orientation of the alkene and the olefin 2 different kinds of products are obtain 1 is this the other is this and of the 2 orientation what has been observed is the ones which are sterically stable is the one which is favored and this product is the favored product for these transformation.

So regio and stereo selective synthesis this is both regio and stereo selective synthesis. So with these we come to the end of today's lecture where we seen taken 3 examples of these kind of eneyne metathesis examples. And all of them has been worked out with ene first pathways where that is first reacts with the olefin and then in today's lecture we have worked out at the different pathways arising from the orientation of the carbene metal complex and the alkyne.

And depending on the different orientation different products were performed and this product ratio is morally guided by this sterics. So one which gives the minimum steric hindrance is the one which predominates in the end. So we with these we come to an end of today's discussion of eneyne metathesis examples. And we are going to take up this reaction in bit more details and few more examples as we discuss eneyne metathesis reaction in the next class. Till then thank you for being with me and hope to see you in the next class goodbye.