Transition Metal Organometallics in Catalysis and Biology
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Module No # 05
Lecture No # 32
Ring Closing Ene yne metathesis (RCEYM) (Part – 1)

Welcome to this course on transition metal organometallics in catalysis and biology. Today we would be talking about ring closing ene yne metathesis reaction in short RCEYM. Now this discussion on ring closing ene yne mechanism has been a discussion that has been going on in the past few lectures where we have tried to characterize this particular type of reaction. And what we have learned is that the ring closing in ene yne metathesis reaction they occurs first in high dilution conditions because these are in trimolecular reactions whereby under dilute conditions the competing in trimolecular reaction like cross metathesis reactions for the alkene and alkyne substrates are suppressed.

Also what we have learnt in our earlier discussion is the fact that this ene yne mechanism metathesis reaction mechanism proceeds via ene first pathway. Whereby the metathesis occurs on the alkene first then subsequently go moves on to alkyne. The reason for this is that if the reverse were to take place that if it is aware to proceed by alkyne first mechanism then the regio selectivity is lost then what is observed in terms of the with regard to the product formation. So today we are going to take a look at some more examples of ring closing ene yne metathesis reactions or RCEYM.

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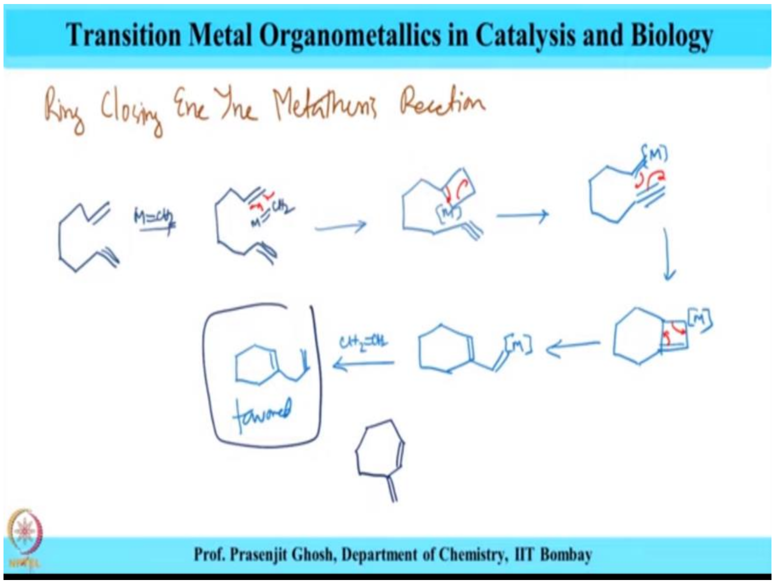

Transition Metal Organometallics in Catalysis and Biology

Ring Closing Ene Yne Metathesis Reaction

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Ring closing ene yne metathesis reaction so this is illustrated for the substrate shown given below for the catalyst CH2. Now the reaction would proceed by forming the corresponding metallacyclobutane species as is shown by here. This active species would react with in the alkene first pathway giving the metallacyclobutane intermediate as shown over here and then that would also undergo rearrangement as it shown here to give the active species like this.

Now that would then react with the alkyne in the fashion shown over here to give this intermediate. Now these can then undergo rearrangement as shown here to give and that in presence of another olefin would give the desired compound. So this formation of this is favored. So this is another example by which this pathway is favored. There are some possibilities or other possibilities like formation of a semi membered ring as is shown here something like this this it is not observed. So the favored product is what is shown over here.

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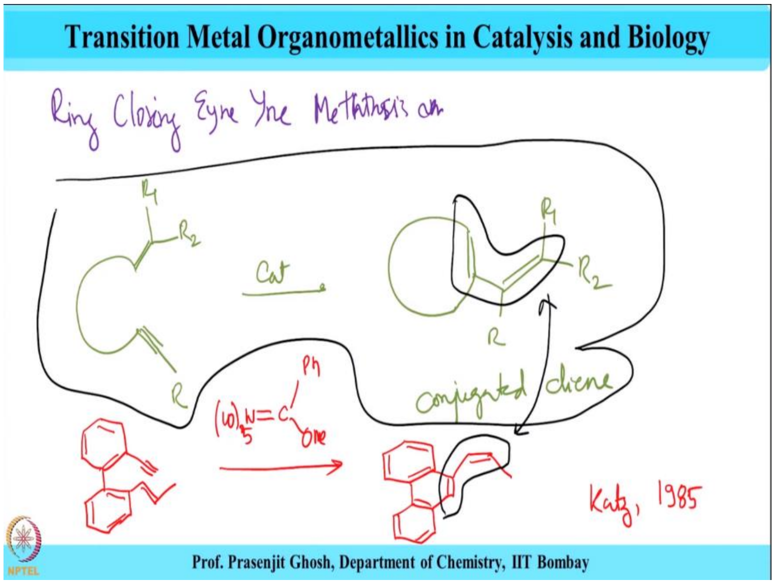

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Ring Closing Eyne Yne Methathesis an

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So we are going to take a look at some more examples of this ring closing ene yne mechanism ene yne metathesis reactions and this we have worked out in some examples and this in short can be represented by a substrate having an alkyne as well as an olefin. And this in presence of catalyst which is a metal carbene species the product is a diene of the type R1 and R2. So this is conjugated diene of this formula. So in the past lectures we have taken look at several of these kind of reaction.

We are going to take a look at few examples of this type of chemistry as is shown over here there is a biphenyl substrate that in presence of tungsten carbene Fischer type of complex. The product which formed thus is so this was reported by professor Katz in 1985. And what this reaction shows is the fact that this moiety this contributed moiety is formed in the product as well and can be seen over here. So this the above is a general representation of these ring closing ene yne metathesis reaction.

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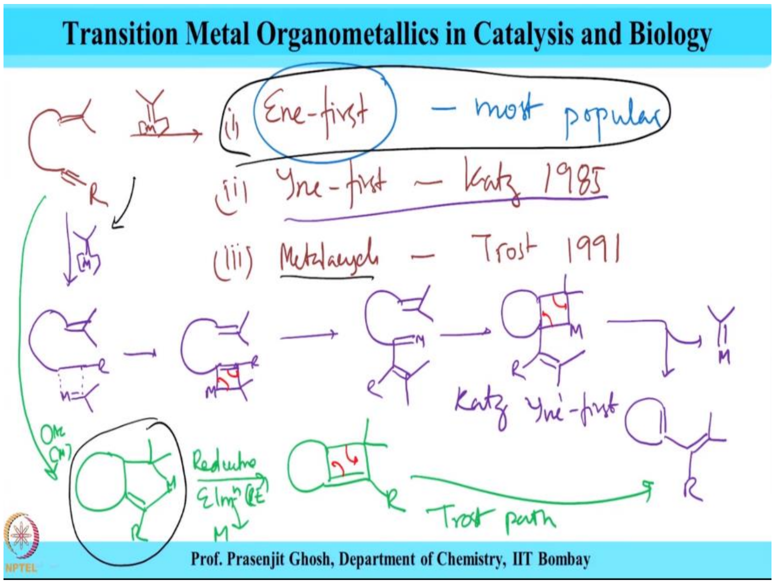

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So are just going to take a look at a mechanism cartoon mechanism proposed for these kind of substrates which is shown over here this R. Then R reacts with the metal catalyst now there are 2 possibilities that this can undergo ene first mechanism or undergo a yne first mechanism. And there is also a possibility that though possibility that there can be a metallo cycle formation mechanism. So there are the proof for the or support for the yne first mechanism was given by Katz in 1985.

And the Trost proposed this metallocycle mechanism in 1991. However the most popular mechanism (()) (13:19) is the ene first mechanism and that is the one which is now believed to be gaining (()) (13:33). So let me just show that the mechanism proposed by Katz which is the ene first mechanism and Katz and the one that is shown by the professor Trost as well. So in the yne first mechanism was first proposed by the Katz it is supposed to attack the yne first by giving the metallacyclobutane that further giving then it is attacking the olefin R.

So this would result along with the product R. Now in the Trost mechanism what is said is so this is the Katz yne first mechanism which is this. And the Trost mechanism is this in present of acetate and the metal would give a metallocycle which would be give which will undergo deductive elimination and release the metal to give these metallacyclobutane compound that would then undergo rearrangement to give the desired product. So this is the Trost pathway apart from ene first mechanism which we had discussed earlier.

So even though the ene first mechanism is by for the most popular one there are possibility of yne first as is shown over here where alkene getting reacted with the metal catalyst and the other is the metalacycle as proposed by Trost these 2 mechanism have been proposed for this alkene alkyne metathesis reaction. However they have not met with much success though.

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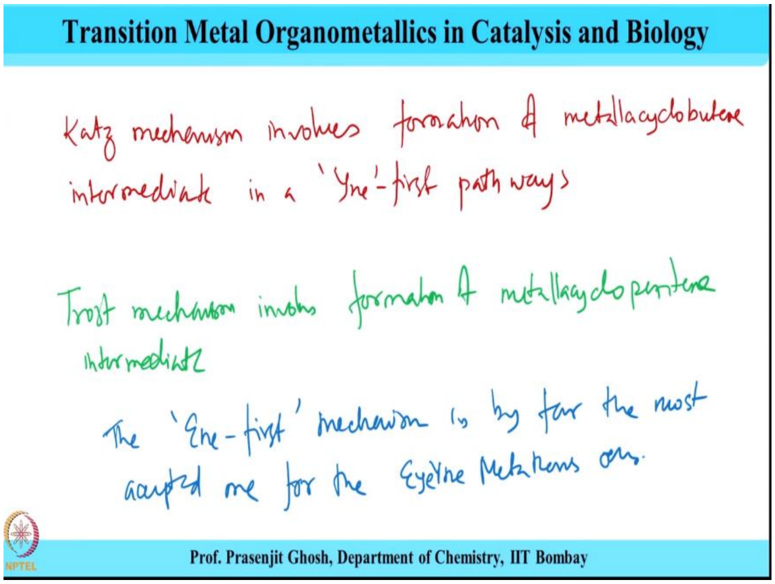

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Katz mechanism involves formation of metallacyclobutene intermediate in a 'Yne'-first pathways

Trost mechanism involves formation of metallacyclopentene intermediate

The 'Ene-first' mechanism is by far the most accepted one for the Eneyne Metathesis rxn.

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So Katz mechanism involves formation of metallacyclobutane intermediate in yne first pathway. Whereas Trost mechanism involves formation of metallacyclopentene intermediate and however they are different. However are the most popular the ene first mechanism is by far the most accepted one for the ene yne metathesis reaction.

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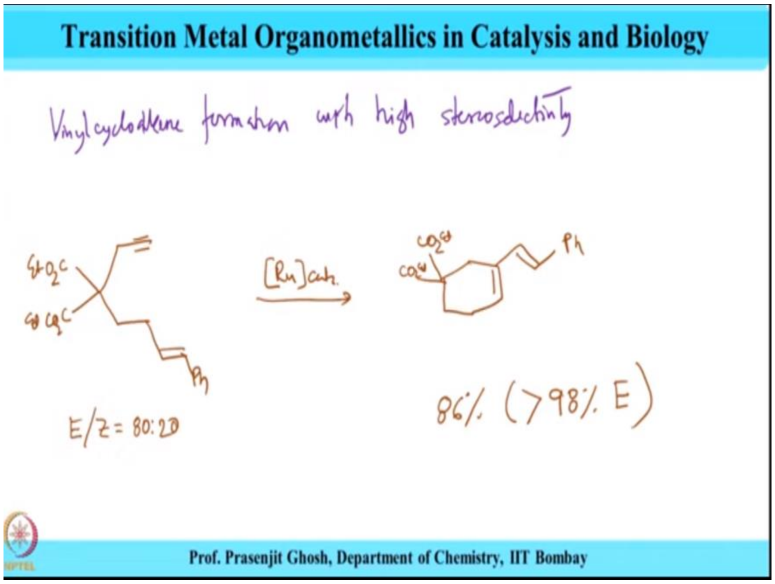

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Vinylcycloalkene formation with high stereoselectivity

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So proceeding further we have a nice example of vinyl cycloalkanes are formed vinyl cycloalkanes formation with high stereo selectivity. This is explained for the in the example CO2 Et this has a E z ratio 80 is to 20 E z ratio in presence of ruthenium catalyst it provides makes the 6 membered ring with these conjugated olefin in high yields it is 86% yield and greater than 98% E olefin. So this is a highly selective way of synthesizing this vinyl cycloalkanes ring using these ene yne metathesis reaction.

So the major drawback despite the successfully utility of these reactions that we have covered the major drawback of this eneyne reaction as discussed earlier is the formation of cross the other metathesis product like the mmm drawbacks homo dimeric products.

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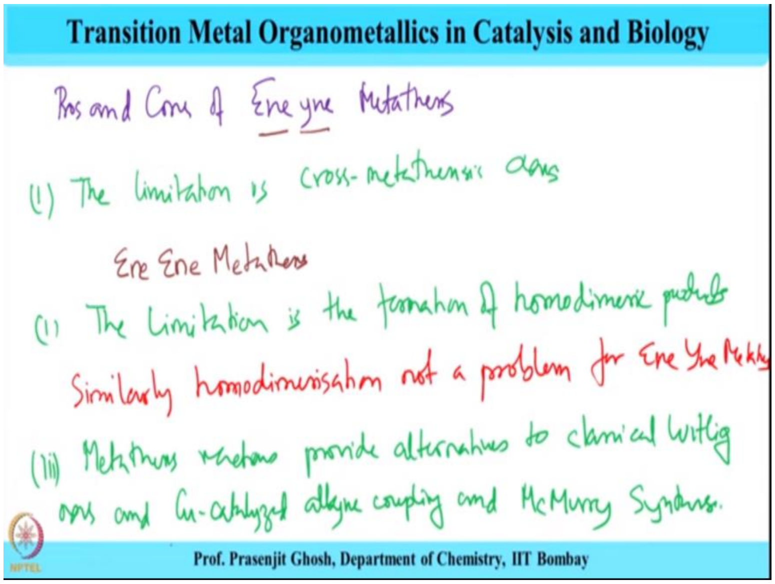

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Pros and Cons of Ene yne Metathesis

(i) The limitation is cross-metathesis rxns

Ene Ene Metathesis

(i) The Limitation is the formation of homodimeric products

Similarly homodimerisation not a problem for Ene Yne Metk

(iii) Metathesis reactions provide alternatives to classical Wittig rxns and Cu-catalyzed alkyne coupling and McMurry Synthesis.

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So pros and cons of eneyne metathesis the limitation is cross metathesis reaction. So this is the limitation now one thing to note here that the in accordance with ene yne metathesis where there is an olefin and alkyne which undergoes metathesis there also reaction which are ene ene metathesis. And the limitation for these ene ene metathesis the limitation is homo dimeric product is the formation of homo dimeric products.

Similarly homodimerization is not a issue for ene yne metathesis. Similarly homodimerization not a problem for ene yne metathesis. And one major important feature about metathesis reaction is they provide viable alternative to many other reactions like Wittig reactions or McMurry synthesis. Metathesis reaction provide alternatives to classical Wittig reaction and copper catalyzed alkyne coupling and McMurry synthesis.

So with these we come to end of today’s discussion on ring closing ene yne metathesis reaction. What we have observed in today’s class is that we have looked at a various mechanistic pathway which has been proposed for explaining ene yne metathesis reaction. To begin with we had already in earlier class looked at ene first mechanism path pathway in which the alkene undergoes the metathesis first.

And in today’s lecture we have looked at two other proposed common pathway one is the yne first pathway was proposed by Katz in which the metathesis of the alkyne is first proposed. Though we had already discussed that this suffers from limitation because of loss of studio regio selectivity because of isomerization process that may happen. And beyond Katz pathway say that another proposed pathway had been by Trost in which 5 membered metallacyclopentane pentene has been proposed.

But these 2 mechanisms has not found round in compared in presence of the ene first mechanism which we have discussed in details. We have also looked into the variety of yne metathesis in terms of we have looked to a new form called ene yne metathesis and what had seen that cross metathesis is the problem for ene yne and homodimerization is a problem for ene ene metathesis. However for ene yne metathesis homodimerization does not play much important role.

At last lastly to summarize this metathesis reaction what we had noted is the metathesis reaction provide a nice alternative to many classical reactions in organic chemistry like Wittig coupling or copper catalyzed alkyne coupling or McMurry synthesis. So with these we come to an end of today’s class. I once again thank you for being with me in this lecture and I look forward to discussing this ene yne metathesis in bit more details when we meet in the next class. Till then goodbye and thank you.