Transition Metal Organometallics in Catalysis and Biology
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Module No # 07
Lecture No # 33
Ring Closing Ene yne Metathesis (RCEYM) (Part -2)

Welcome to this course on transition metal organometallics in catalysis and biology in continuing with our earlier discussion we would be looking at examples of ring closing ene yne metathesis reaction in short this reaction is called RCEYM ring closing ene yne metathesis reaction. And then will try to finish up all the related examples with regard to this particular reaction and then if we have time we are going to start a another new topic another new interesting reactions which are alkene and alkyne oligomerization reaction.

Now in keeping with the theme of this course which are intended to highlight all the industrial scale applications of organometallics reaction and catalysis in particular this alkyne and alkene oligomerization reaction is another noble prize award winning discovery that we ate going to take up next after olefin metathesis which was also awarded as noble prize. So now we will go back to our discussion on ring closing ene yne metathesis reaction.

We had looked into several examples in the earlier lecture about ring closing ene yne metathesis reaction. What we have in a just what we have learned so far is that ring closing ene yne metathesis reaction is a intra molecular reaction where the substrate happens to have both the olefin as well as the alkyne bond.

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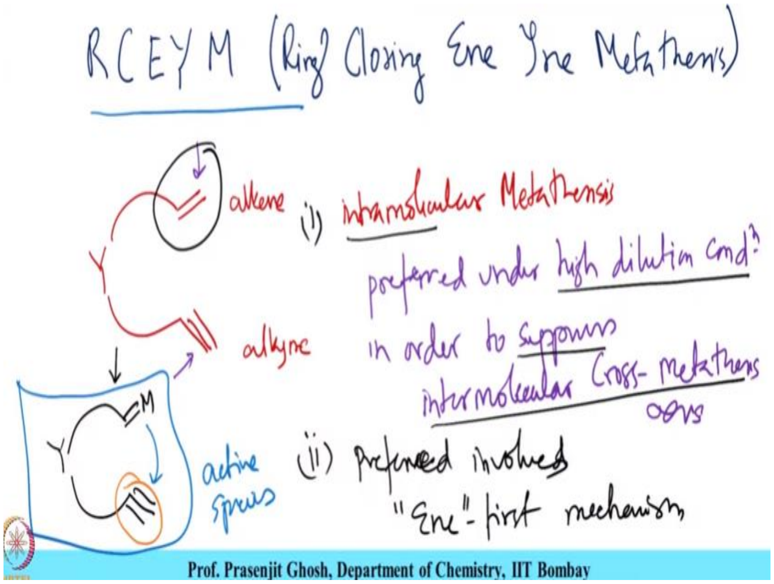

RCEYM (Ring Closing Ene Yne Metathesis)

(i) intramolecular Metathesis
preferred under high dilution cond^n
in order to suppress
intermolecular Cross-metathesis occurs

(ii) preferred involves
"Ene"-first mechanism

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So to in short ring closing ene yne metathesis are ring this is reaction this reaction what we have learned in short is that the are the substrate as both the alkene and the alkyne components and the reaction is intra molecular metathesis reaction and hence the preferred mode of reaction is that it is preferred under high dilution conditions in order to suppress intra molecular cross metathesis reaction.

And these cross metathesis reaction may occur between the alkynes 2 of these molecules alkynes it can be alkyne cross metathesis inter molecular cross metathesis or even alkene inter molecular cross metathesis and this is pretty suppress by performing this RCEYM reaction under high dilution conditions. And the last thing is these are important properties that we have been learning about these RCEYM first is that this is the intra molecular reaction preferred under high dilute conditions and suppress the cross metathesis condition.

The second thing is that the favorable pathway or preferred pathway involves Ene-first mechanism which means that the active species is formed on the olefin first and the active species is the metal carbine species as it shown over here and that further reacts with the alkyne subsequently this reacts with the alkyne subsequently to give the corresponding RCYM product. And this is the active species for this ring closing ene yne metathesis reaction.

So this is exactly a few points that we take home from our discussion on ring closing ene yne metathesis reaction. In these regard we have looked into other possibilities for example we had looked into the possibility of reaction happening in the alkyne or at this site alkyne site giving the active species but and that mechanism is called ene first mechanism. But you know we have also noted that ene first possibility will have lot of regio isomers so there is lack of regio selectivity whereas these reactions as observed are highly selective which sort of points to the ene first mechanism.

So in this context we have discussed various other possibilities which have been proposed but have not gained possibility with regard to the mechanism active species as well as mechanism in which these reactions are carried out. Now continuing with our discussion on ring closing ene yne metathesis. Today we are going to look at 2 more examples of RECYM reaction but they are taken in a context of more complex maneuver with regard to organic synthesis particularly tandem reactions which involves RCEYM along with other reaction.

For example it can might as well as be a cyclo addition or other reactions which in tandem with RCEYM some complex substrate has been obtained. So let us start with these examples that I have been referring to.

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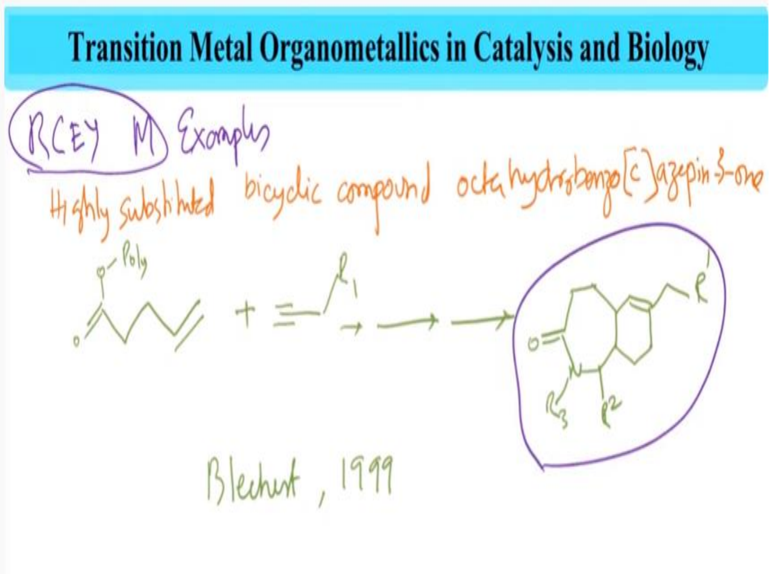

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RCEY M Examples

Highly substituted bicyclic compound octahydrobenzo[c]azepin-3-one

Blechert, 1999

So in this let us take a look at this example of tandem RECYM in which there is a cyclo addition reaction proceeding along with the ring closing metathesis reaction examples. The one that we would be referring to have been used for synthesizing high substituted bicyclic compound octa hydro benzo c azepin 31. So these is given as in over here the reaction is shown over here R1 and after several maneuver the final product is this compound and this complex synthesis was reported by Bleckert in 1999.

So these synthesis very nice way of making this complex molecule involved using these 2 strategies once RC ring closing RC involved this ring closing RC in ene yne metathesis reaction. This involves ring closing ene yne metathesis reaction this complex example was synthesized using this ring closing ene yne metathesis along with tendon cyclo addition reaction. So we are going to take a look at the mechanism for this formation as is given below.

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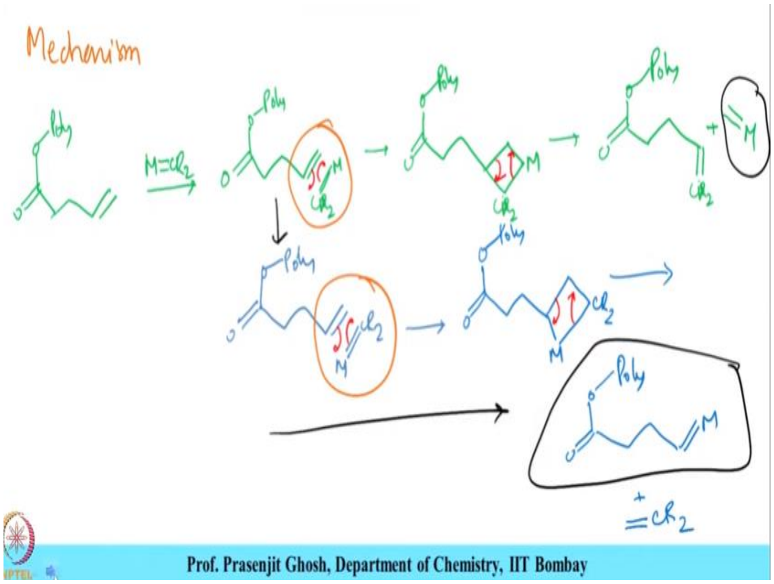

This involve first the reaction of the substrate some polymer support these reacting with CO2 CR 2 and the reaction proceed as shown here and then and this would give the product as it shown here. Now these is not active species this is the active species but will not propagate so then the reaction would proceed the one which would be necessary would be the one that would proceed along the other confirmation.

Please note the confirmation over here as over here just the reverse now these would then react further to give and now that would rearrange to give the product. So this the point to note that these possibility this is the correct pathway that give the active species on this substrate. So the next step this involves the reaction of the substrate for with further the product and this is shown in the next slide.

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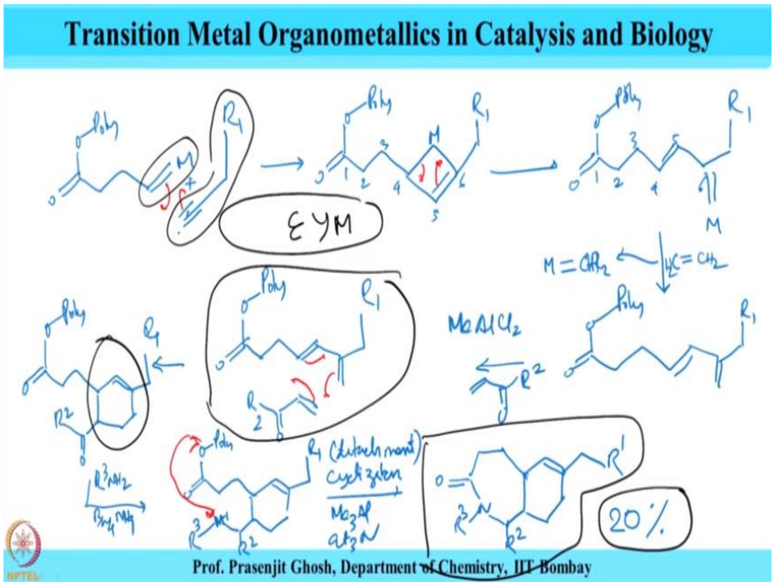
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Now this substrate would then react with the alkyne substrate which is R1 to give as is shown here. Now these would subsequently undergo rearrangement as is shown here so double bond between 4 and 5 R1. Now these then would react with olefin to give the corresponding metathesis product along with the elimination of CR2 the active species. So once this is formed then this is reacted with methyl aluminum trichloride in presence of this alpha beta unsaturated carbonyl compound R2.

So a cyclo edition reaction follow suit as is shown over here and the reaction proceeds to give these product which then is reacted with amine in (()) (20:55) NH4 reagent to give this amide NH R3 and finally this cyclization with trimtheyl aluminum and triethyl amine cyclization involves this reaction with this amine over here to un-followed detachment from the ring give the desired product as it shown here in R3 R2 R1 in 20% yield.

Now these is a very interesting reaction and even though the yield 20% seems low but in the context of such a complex molecule 7 member 6 member bicyclic amido function of the compound so such a complex molecule being formed in a multiple sequence standard step sort of speaks well about this yield of even 20% which otherwise miss in very low but this is not trivial in this particular case because such a complex molecule has been formed.

Now another important highlight of this reaction is that it undergoes these ene yne metathesis reaction ring closing ene yne metathesis reaction this reaction happens in the first half and then these cyclo addition reaction which happens in the reaction of the six membered ring and that sort of shows the beauty of this reaction. So this to put this 2 reaction which has happened they are more appropriately they are called ene yne metathesis not the ring closing because you the 2 substrates are not on the alkene and the alkyne moiety are on 2 different substrates.

So this is intermolecular ene yne mechanism metathesis reaction so this is the intra molecular reactions and then as the alkene and alkyne are on 2 different substrates. So with these we come to an end of today's discussion where we have taken up an example and work it out showing the different orientation in which the metal carbine species may react with the substrate and what we have seen is tandom reaction of cyclo addition as well as ene yne metathesis with regard to the earlier discussion on ring closing ene yne metathesis reaction and how these active species lead to a very active product which is shown over here even in 20% yield.

So with that we come to conclusion of today's lecture were we have seen tandem reaction as it proceeded by these ene yne metathesis and cyclo addition reaction we are going to take up bit more detail another example interesting example if these ene yne metathesis reaction when we meet next on this lecture series till then good bye and thank you.