**Transition Metal Organometallics in Catalysis and Biology**
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**Lecture - 27**
**Ring Closing Metathesis (Part-3)**

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been discussing ring closing metathesis reaction in details in the last few lectures and what we have noticed over and over again through various examples that we have studied that ring closing metathesis indeed is a very powerful reaction for constructing large macrocyclic compounds.

And what we have also observed that whenever, there are possibilities of several types of ring closing metathesis occurring on a substrate having multiple alkene moieties then the one which is giving larger macrocycle is the one which is favored and this is easily explained by the reason that the rings with less ring strain are the ones which would be a preferable in the course of ring closing metathesis reaction.

So continuing with our discussion on chiral form of ring closing metathesis more particularly better known as asymmetric ring closing metathesis or ARCM. We are going to be looking at some more examples of ARCM in this lecture and then continue further along those lines.

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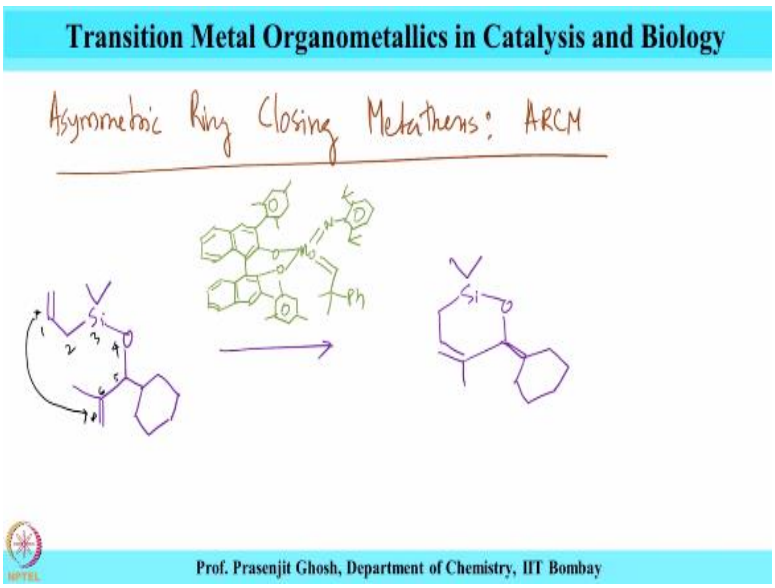

So asymmetric ring closing metathesis or ARCM this is what it is properly known as. And we are going to be looking at a particular example using a chiral catalyst. And this also uses molybdenum imido carbene complex with elaborate ligand scaffold as is drawn over here. This has a bulky mesityl moiety bound to molybdenum with two (()) (3:53) phenyl imido and the carbene moiety is with dimethyl phenyl substituents as is shown over here.

And these catalyst facilitates ring closing between these two olefins resulting in six membered cyclic compound and the corresponding product thus becomes as is shown over here. Now the scope of these ring closing metathesis is further expanded in a next example that we are going to look at, which involves ring closing metathesis as well as cross metathesis.

So these are tandem reactions where two reactions happen. The first one obviously is the cross metathesis followed by ring closing metathesis which results in larger cycle. And another interesting aspect of this example is that depending upon the reaction condition, one particular product is favored over the other. So we are going to take a look at this nice examples of tandem cross metathesis and ring closing metathesis reactions.

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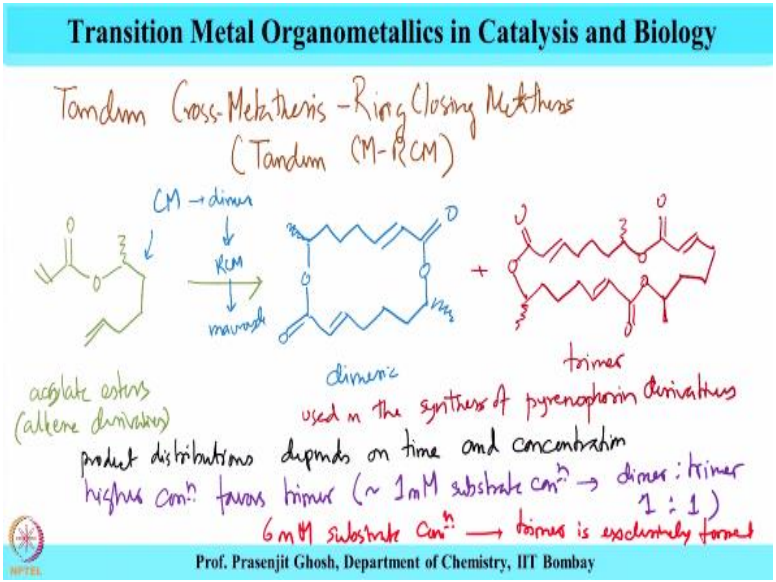


Which in short is known as tandem CM-RCM reactions. So this is nicely illustrated in the following substrate. These are acrylate ester or alkene derivatives. So upon reaction it undergoes cross metathesis followed by ring closing metathesis to give

large macrocyclic structures as is shown over here. This is a dimeric structure. So in this dimer formation what happens is first the reaction of two of this unit happens through cross metathesis.

And then to give the dimer and then RC and ring closing metathesis to give the macrocycle. Now the reaction can also give a mixture where a trimer is obtained along the same pathway. This is the trimer and these are useful compounds and used in synthesizing of pyreno polyphene derivatives used in the synthesis of pyrenophorin derivatives and the interesting aspect is that the product distribution is dependent on time and concentration. Product distribution depends on time and concentration.

For example, higher concentration favors trimer over dimer and example at one millimolar substrate concentration that is dimer to timer ratio is 1:1. However, at 6mM substrate concentration trimer is exclusively formed. So this is an interesting reaction where we see that two metathesis reactions occurring in tandem sequence together one by in a sequential order tandem order one by one.

So we see that for this acrylate ester substrates, we see cross metathesis between the substrates giving a dimer and then the RCM giving a macrocycle. So these macrocycle can be derived from dimeric structure as well as from a trimeric structure and these are useful compounds required for the synthesis of pyrenophorin derivatives.

But what is more interesting is to note over here that the formation of these dimer and the trimeric structure is very much dependent on the substrate concentration used in the reaction. For example, higher substrate concentration favors the trimer formation and this is illustrated by the fact that at one millimolar substrate concentration, both the dimer and trimer are formed in 1:1 ratio.

However when one goes to a higher concentration for example, say to 6 mM substrate concentration then one finds formation of timer to be exclusive. So this is a nice example of tandem cross metathesis ring closing metathesis reaction or in short called tandem CM-RCM reaction.

So we are going to look at some more tandem reactions for example, the next one that we are going to look at is ring opening ring closing metathesis reaction or it is called RO-RCM or in short ring rearrangement metathesis reaction or called RRM reaction.

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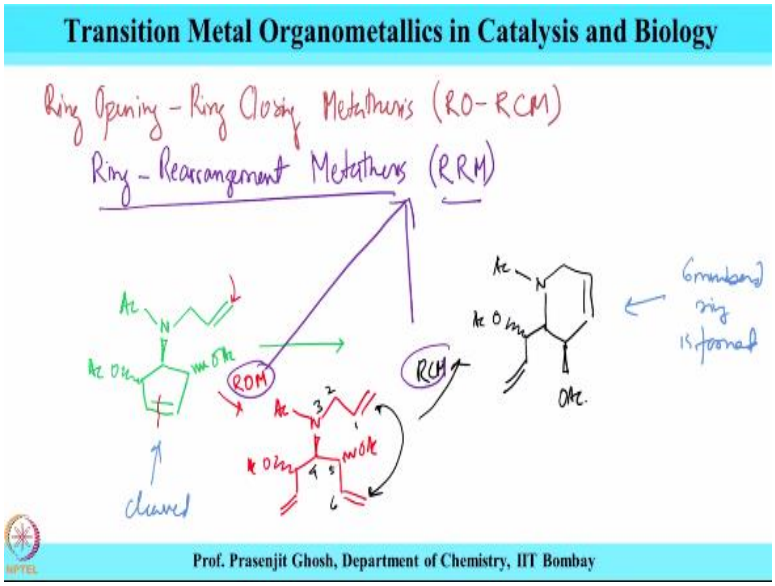


So ring opening ring closing metathesis RO-RCM or ring rearrangement metathesis or RRM reaction. So this also is a interesting reactions, where we would see that two reactions are happening, ring opening as well as ring closing. So this is observed in case of the cyclic alkene derivative. So the first thing is ring opening and where the ring opening occurs in the cyclopentane ring as it is shown over here followed by a ring closing that occurs with the alkene generated from these two with that.

So the first step is one can think of ring opening metathesis which will sort of give and then the next step would ring closing. So that would involve this olefin reacting with this giving a six membered ring and finally getting a structure which would be okay. So what if one were to look at the outcome is that smaller five membered ring is cleaved and the six membered ring is formed. So no this is simultaneous to metathesis reaction occurring.

The first is ROM and next is RCM and together these two reaction, this ROM and RCM together is referred to as RRM or ring rearrangement metathesis reaction. So this is a nice example of two sequential metathesis reaction that occur to form six membered ring. So we are going to also look at some more examples of this ring opening ring closing RRM reaction as we proceed through today's discussion.

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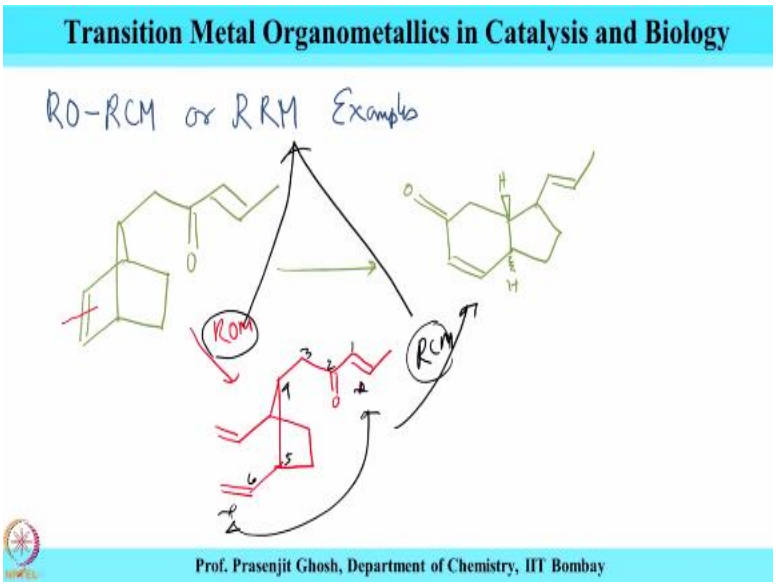


RO-RCM ring opening ring closing metathesis or RRM ring rearrangement metathesis examples. Here is a nice example in which a norbornene fragment undergoes RO-RRM kind of rearrangement. And here what happens is that first the ring opening takes place and then the ring closing occurs resulting in the following bicyclic compound which is shown over here.

So the first is the ring opening of this to give and then ring closing between one of these olefins to give this macrocycle five membered and six membered macrocycle as is shown over here. So this is RCM and together they would represent RRM which is ring rearrangement reaction. We are going to take a look at another example of this RO-RCM and RRM.

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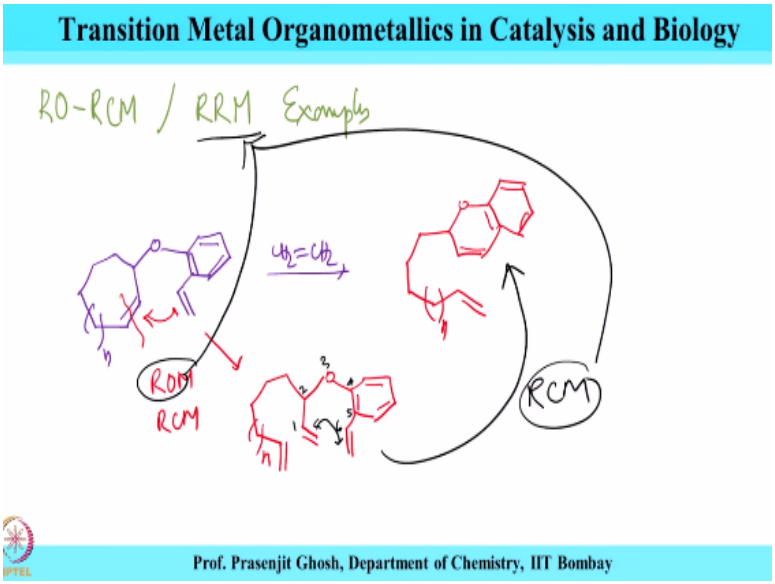


Ring opening ring closing metathesis or ring rearrangement reaction examples and this is observed for this cyclic compound styryl-allyl-ethyl compound as is shown over here. And this in presence of ethylene and catalyst gives first the ring open product along this and then the RCM product between this. So ROM then RCM to give the following product as is shown over here.

So this is another nice example of ROM and RCM occurring over here. So if one sort of looks at it, so during the process of ROM, so in the process of ROM this would open up. And then there will be ring closure, which will be affected by these two olefin resulting in the six membered ring as is shown over here. So this is RCM and this is ROM and together they would be called as RRM or ring rearrangement reaction.

So what we had done today is that we have looked at ring closing reaction, various aspects of ring closing reaction including tandem reactions of ring closing reactions with other metathesis reaction. In particular we have looked at cross metathesis ring closing reaction or CM-RCM or we have looked at also various examples of ring opening ring closing metathesis or RO-RCM.

In short they are also popularly referred to as ring rearrangement reaction. So with this we come to an end of our discussion on ring closing metathesis reaction. We have looked into various types of ring closing metathesis reaction, various types involving the achiral versions. Then we have also looked into the chiral variety.

What is prominent in this reaction is the fact that ring closing metathesis reactions usually are extremely useful for preparing large macrocyclic compounds where the ring strength is not too acute and hence, these reactions are favored. We have also seen that ring closing metathesis can be applied with other metathesis reactions for example, cross metathesis reactions, as well as ring opening ring closing metathesis reactions for preparing target as molecules with scaffolds which are used for useful for other special kind of applications.

So with this, we come to the conclusion of today's lecture, where we have finished our discussion on ring closing metathesis reaction particularly, we have observed that how these reactions have been put in use, and we have also looked into their tandem variety. So with this I conclude our discussion on ring closing metathesis reaction. We are going to be taking up another new topic, which is alkyne metathesis when we meet next for the, for this course.

This we are going to be talking about alkyne metathesis. So far we have restricted on all types of metathesis reactions, which are known for olefins, but we are going to expand the domain of metathesis reaction and we are going to be looking at alkyne metathesis reaction which also by its own right and merit falls in the overall class of metathesis reaction.

So with that I once again thank you for being with me and I look forward to being with you when we take up this alkyne metathesis in the next class. Till then goodbye.