Transition Metal Organometallics in Catalysis and Biology
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Lecture - 28
Alkyne Metathesis

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. In the last few lectures, we have been discussing about olefin metathesis reaction, we have looked into various forms of or various types of olefin metathesis reaction, that starting from cross metathesis acyclic diene metathesis polymerization ADMET.

Then we looked into ring opening metathesis as well as ring opening metathesis polymerization ROM, ROMP. Then we have looked into ring closing metathesis RCM. We have also looked into various kinds of tandem reactions, metathesis reactions starting from cross metathesis, ring closing metathesis or which is popularly known as CM-RCM.

As well as we have looked into several examples of ring opening and ring closing metathesis which is in short, popularly known as ring rearrangement metathesis or RRM. So having completed our discussion on alkyne metathesis, we move on to another topic, which is alkyne metathesis. Now these alkyne metathesis is similar to that of alkene metathesis and falls in the subclass of metathesis reaction.

And we are going to be discussing about alkyne metathesis and its examples and application in more detail as we proceed through this class. So as we proceed further, we are going to look at some of the examples of this new type of metathesis which is alkyne metathesis reaction.

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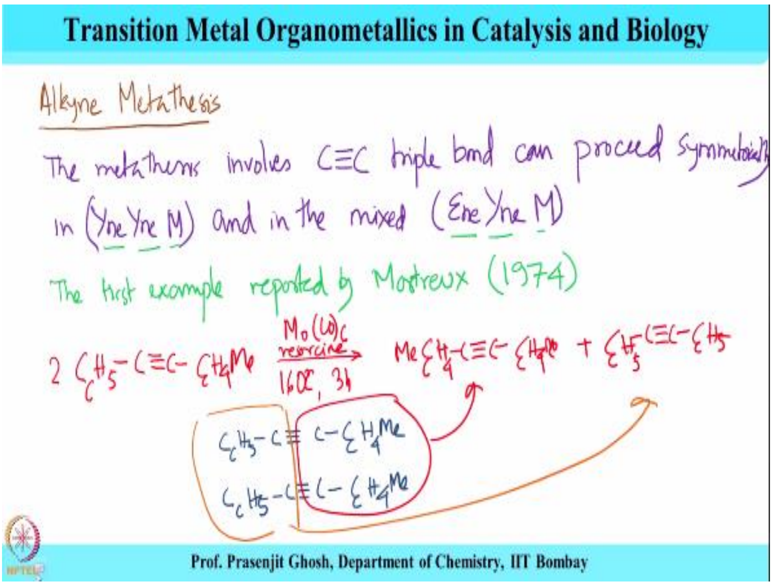

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Alkyne Metathesis

The metathesis involves C≡C triple bond can proceed symmetrically in (Yne Yne M) and in the mixed (Ene Yne M)

The first example reported by Mortreux (1974)

$$2\ C_6H_5-C\equiv C-C_6H_4Me \xrightarrow[160^\circ C,\ 3h]{Mo(CO)_6,\ resorcine} MeC_6H_4-C\equiv C-C_6H_4Me + C_6H_5-C\equiv C-C_6H_5$$

$C_6H_5-C\equiv C-C_6H_4Me$

$C_6H_5-C\equiv C-C_6H_4Me$

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This as the name suggest alkyne metathesis involves metathesis of carbon-carbon triple bond, involves and can proceed symmetrically in Yne Yne metathesis. So which is a triple bond triple bond metathesis and in the mixed form Ene Yne metathesis. So this is an interesting that there is a great extent of versatility of this metathesis of triple bond. It can be a pure, it can be of pure Yne Yne metathesis type, or it can also be Ene Yne metathesis type.

The first metathesis reaction was reported by Mortreux in 1974. First example Mortreux in 1974. And the example is given by. So two molecule of this in presence of metathesis catalyst which is formed from molybdenum hexacarbonyl and resorcine at 160 degree centigrade and 3 hours giving the metathesis product.

Plus and these can be viewed in terms of cutting and stitching to alkyne fragments similar to which is popularly observed for alkene metathesis reaction in which it seems that cutting and stitching across this triple bond one leading to this fragment and the other leading to this fragment. So this resembles very much the alkene metathesis reaction which one is familiar with.

So we are going to take a look at some more examples of alkene metathesis to get a feel for the pathway in which this mechanism proceeds and also to get insight into the active catalyst, which is responsible for carrying out these alkyne metathesis reaction.

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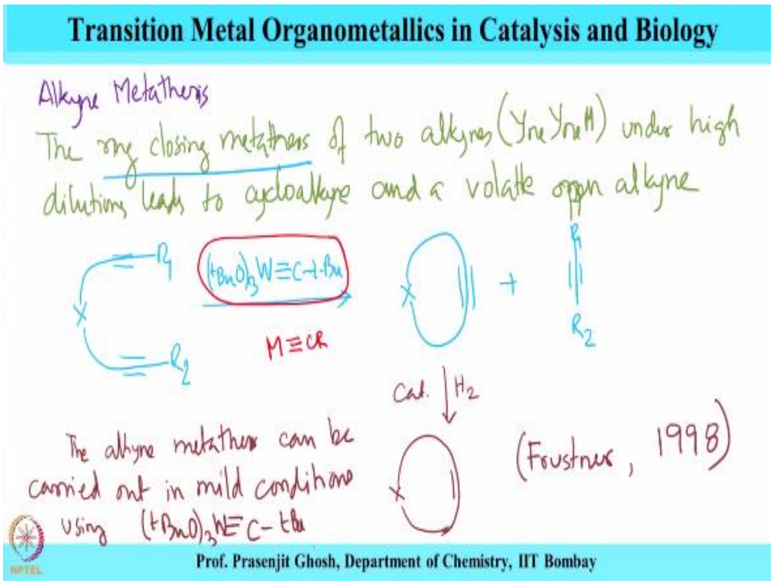

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Alkyne Metathesis

The ring closing metathesis of two alkynes (Yne Yne M) under high dilution leads to cycloalkyne and a volatile open alkyne

(Furstner, 1998)

The alkyne metathesis can be carried out in mild conditions using $(tBuO)_3W\equiv C-tBu$

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The ring closing metathesis of two alkynes usually are done under high dilution conditions to give cycloalkynes and volatile alkyne similar to that of volatile ethylene that we had obtained during the alkene metathesis reaction. The ring closing metathesis of two alkynes Yne Yne M under high dilution conditions leads to cycloalkyne and volatile open alkyne.

The point to note here is the fact that similar to the ring closing metathesis which we had observed for alkanes ring closing metathesis of alkynes are also feasible and this can be seen over here in which cycloalkynes are formed along with an open chain volatile alkyne which drives the reaction forward.

To give an example substrate of the type this shown with R 1 and R 2 in presence of the catalyst tungsten C-t-butyl leads to the cycloalkyne along with open alkyne and the point again to note here is the catalyst for alkyne metathesis is a metal turbine species similar to the metal carbine species, which had been the catalyst for olefin metathesis reaction.

Furthermore, the cycloalkynes so obtained can be readily hydrogenated using suitable catalyst to give cycloalkane. The alkyne metathesis can be carried out in mild conditions using tungsten catalyst and this very nice piece of work was reported by Furstner in 1998. So alkyne metathesis has a parallel with alkene metathesis and also as is observed for alkene metathesis, the ring closing metathesis for alkyne is equally possible.

And here is a nice example in which cycloalkyne was prepared using ring closing alkyne metathesis which when hydrogenated give the cycloalkene along with the formation of an open alkyne during the process of ring closing alkyne metathesis. Well, we are going to take a look at some more examples of alkyne metathesis particularly the notable ones in which this initially a alkene metathesis been performed, followed by alkyne metathesis.

And subsequently a reduction of the alkyne so formed to get the desired product. So this particular example that we are going to be talking about is kind of interesting in the sense that it has two different kind of metathesis, first the alkene metathesis followed by alkyne metathesis and then subsequently a reduction with hydrogen.

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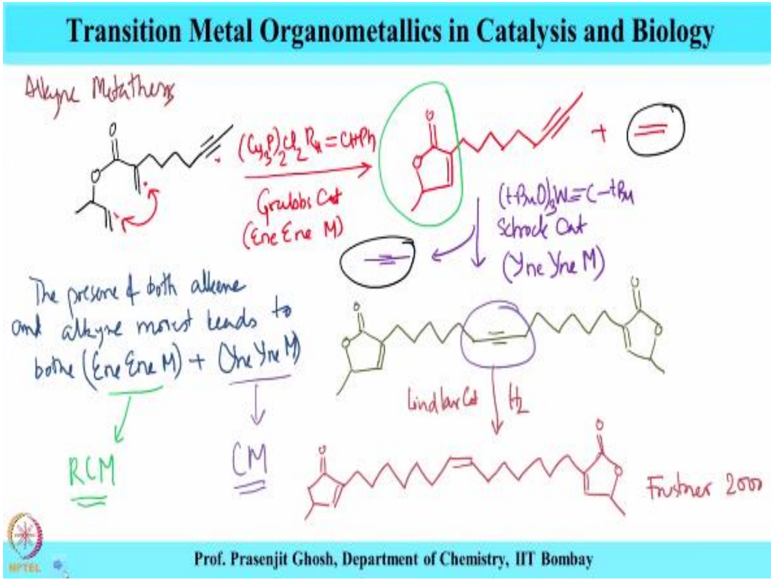

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The presence of both alkene and alkyne moiety leads to both (Ene Ene M) + (Yne Yne M)

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So for this substrate note that this substrate has several olefinic bonds, which is marked per here, as well as an alkyne bond and hence two different catalysts are used one for olefin metathesis followed by the next one for alkyne metathesis to get to the desired product. So this is an example where very nice interplay of different metathesis catalyst been used cleverly to get to the final product.

The first is the Grubbs catalyst. And what first attempt is his first attempted is Ene Ene metathesis which sort of implies the metathesis between these two double bond and the catalyst used is to give this complex. Now after the first Ene Ene metathesis has been carried out, the next comes the second metathesis which is the alkyne metathesis.

And for this different catalyst tungsten alkyne catalyst which is Schrock catalyst and these catalyst carries out Yne Yne metathesis and the catalyst is and in this case, when this metathesis occurs between two of the substrate then the alkyne, open alkyne, which is liberated is dimethyl acetylene.

Similarly, in the previous case the open alkyne liberated would have been ethylene and the liberation of these open alkynes for example this ethylene in the former case and the methyl acetylene in this previous case they provide the required driving force for this Ene Ene metathesis as well as Yne Yne metathesis reaction.

Now this upon undergoing alkyne metathesis gives the product which is a alkyne and then to this alkyne hydrogenation, subsequent hydrogenations by Lindlar's catalyst provides this d-isomer and this beautiful work was also demonstrated by Furstner as early as 2000. So the main attraction of this work is that the presence of both alkene and alkyne moieties leads to both Ene Ene metathesis plus Yne Yne metathesis.

And this is a nice way of demonstrating that these two catalysts to do not interfere with each other and that they are compatible to each other and then they successfully carry out two different metathesis reaction, one is Ene Ene metathesis and as well as the alkyne one is Yne Yne metathesis. Now if one were to look bit more further then one would realize that the Ene Ene metathesis which has been formed, this actually is a ring closing metathesis because a five membered ring is formed as a result of this Ene Ene metathesis.

And the Yne Yne metathesis, which is reported in the second step that actually is a cross metathesis and which eventually leads to alkyne formation in the middle of the sub product backbone. So these two reaction Ene Ene metathesis Yne Yne metathesis in fact are RCM and CM metathesis reaction that has been successfully carried out towards achieving a particular complex molecule by a series of step and this was cleverly demonstrated by Furstner.

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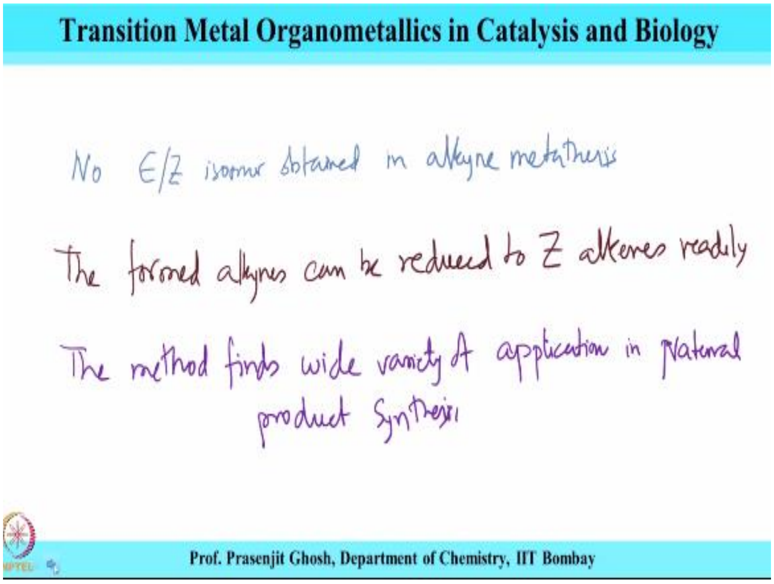

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No E/Z isomer obtained in alkyne metathesis

The formed alkynes can be reduced to Z alkenes readily

The method finds wide variety of application in Natural product Synthesis

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So the main hallmark of this synthesis is no E Z mixture of the final olefin product obtained in alkyne metathesis also the formed alkynes can be readily reduced to Z alkenes, can be reduced to Z alkenes without much trouble readily. The method as a whole finds wide variety of application in natural product synthesis. So this is a very useful method of making alkyne by reacting with different substrates.

And now, we are going to look at some of the examples of some variant which are mixed metathesis which is sort of alkene alkyne metathesis.

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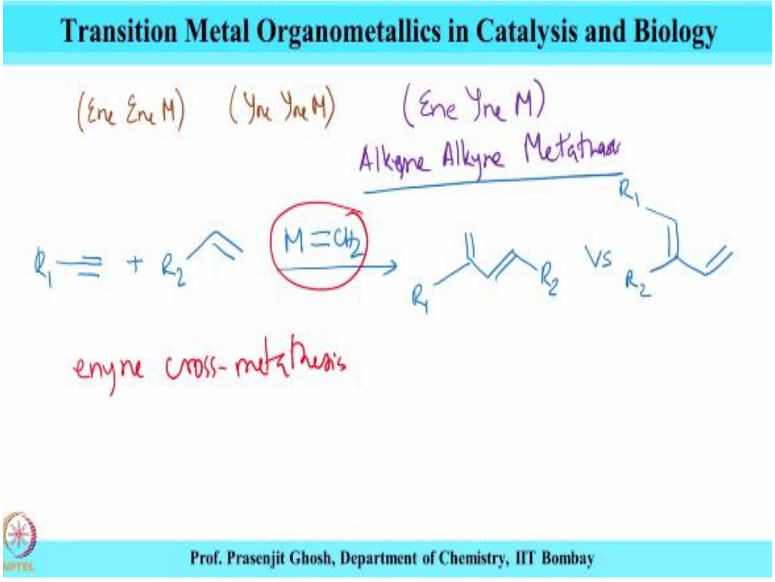

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(Ene Ene M) (Yne Yne M) (Ene Yne M)

Alkyne Alkyne Metathesis

enyne cross-metathesis

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So, so far we have looked into examples of Ene Ene metathesis as well Yne Yne metathesis and what we are going to do now is look into Ene Yne metathesis which is a combination of alkyne metathesis. So this is popularly called as alkene alkyne metathesis. And these are more purer form of metathesis reaction because this involves olefin and alkyne whereas, this involves reaction between olefin and an alkyne together.

So the reaction is beautifully (()) (25:02) reaction this alkene alkyne metathesis is represented by the following substrates which involves an alkyne and alkene and that in presence of a metal olefin compound which is suppose the catalyst provides the desired Ene Yne metathesis product. There are various possibilities and one of such possibilities are shown here. So this kind of reaction in principle in general are called Ene Yne cross metathesis.

One interesting to note about this Ene Yne cross metathesis is the nature of the catalyst, which over here is usually a metal carbene complex which can help in performing this Ene Yne catalysis. So usually metal carbene complexes, which are catalyst for olefin metathesis can also carry out this Ene Yne metathesis involving a olefin and alkyne.

So with this, we come to the end of today's discussion in which we have looked into various types of alkyne metathesis reactions with examples and also looked into a new type of alkyne metathesis which is alkene alkyne metathesis or Ene Yne metathesis. Now things to note over here is that alkyne metathesis runs parallel to that of alkene metathesis and there are several reactions, which are in common for both type of metathesis.

For example, we have looked into one example in which the ring closing metathesis as is observed for alkene metathesis can also be realized for alkyne metathesis with the formation of volatile open alkyne compounds, which drives the reaction forward. We have also looked into alkyne metathesis like cross metathesis which also has a parallel for olefin metathesis where also cross metathesis is possible.

Notable difference initially what we had observed is the fact that the way metal carbene complexes are active species for olefin metathesis for alkyne metathesis metal carbine complexes act as a catalyst and these mainly Schrock kind of catalyst.

So as Schrock catalyst are quite common or more popular for alkyne catalyst, the way Grubbs catalyst is more popular for olefin or alkene metathesis catalyst.

So we are going to be discussing this alkene alkyne metathesis in much more detail, particularly from the mechanistic perspective, how a metal carbene catalyst can participate and carry out both this Ene Yne metathesis reaction. We are going to be discussing that in more detail in the next class. And we are going to take it further and look into various examples and various types of this mixed metathesis or popularly known as alkene alkyne metathesis, that we would be discussing in the next lecture.

So once again, I would like to thank you for being with me in this particular lecture and we are going to be discussing Ene Yne metathesis reaction in bit more detail when we meet next. Till then, goodbye and thank you.