Transition Metal Organometallics in Catalysis and Biology
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Module No # 04
Lecture No # 19
Cross Metathesis (Part -1)

Welcome to this lecture on transition metal organometallics in catalysis and biology and in this series of lecture we have looked into various reactions that we important to catalysis particularly from industrial perspective in terms of industrial scale synthesis and we have been looking at the applications of organometallics chemistry in a big level. Now in these series of lecture in last 2 lectures we have looked into olefin metathesis particularly alkene metathesis reactions.

We have looked at how it was developed the story behind the development discovery development mechanisms and also the various types of metathesis reaction that have been subsequently discovered and put under same umbrella as the class of metathesis reaction continuing further with discussion we are going to be discussing another important topic variant of metathesis reaction particularly the cross metathesis reactions.

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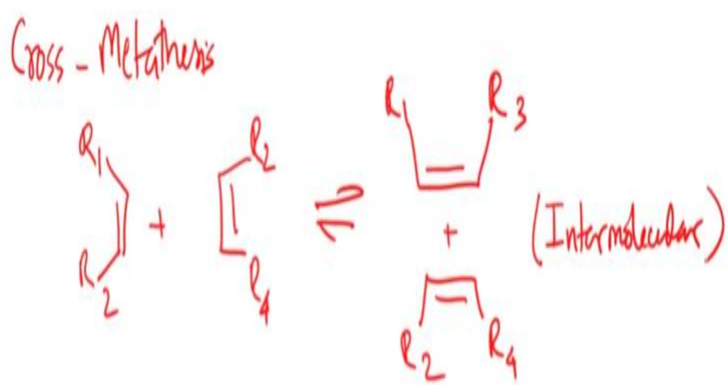

The cross metathesis reaction is given by the following equation and it is represented by so this is sort of intermolecular metathesis reactions. Intermolecular version of metathesis reaction now these cross metathesis reaction the applications of cross metathesis reaction is significant and the development of cross metathesis reaction for industrial purpose application is also very interesting. Now let me just brief overview of the story of how these cross metathesis reaction came into being and particularly for utility in industrial scale applications. Now these all began back in 1960's or 70's 60's particular when people are trying to make these large scale synthesis of olefin's.

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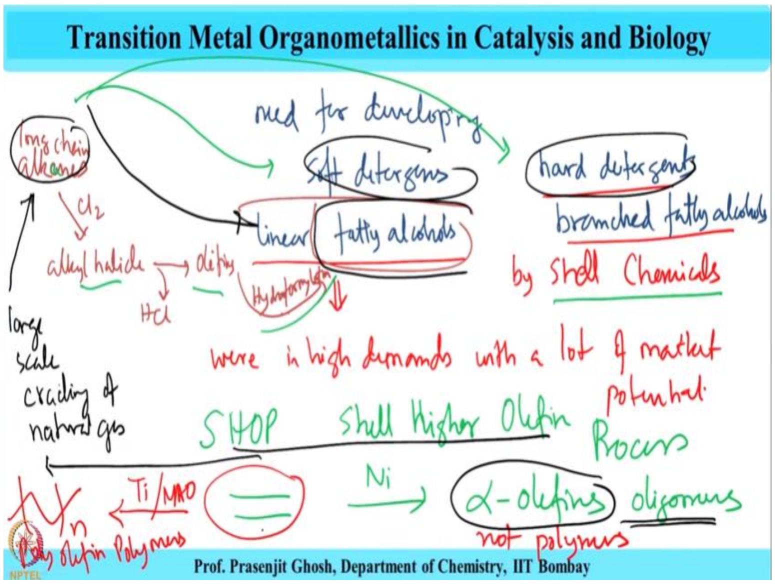

Now the story is starts with the need for developing soft detergents which are nothing but linear chain linear fatty alcohols as opposed to hard detergents which are branched fatty alcohols now these fatty branch alcohols they were sort of being sold by shell development shell chemicals and these hard detergents are branched fatty alcohols a long chain alcohol branched long chains with alcoholic ends these are called long fatty alcohols they were causing a lot of depositions of forms and the rivers the forms and surfactants on the rivers then it was sort of creating a biological ecological havoc.

And there was a need and because of lack of any method of degradation there was a need to develop the soft detergents having linear fatty alcohols. So that is the story starts and fatty alcohols the time were in high demands and had lot of market potential. So they were in high demands with lot of market potential. So the idea was to access long chain fatty alcohol and they primary was being produced from hyfromylation from alkanes in presence of chlorines to give long chain alkanes to give alkylalide that would undergo HCl elimination to give olefin's.

And that olefin's under hydroformlyation's and then subsequently reduction would give this fatty alcohols both linear and the branch. So that was the method at that point of time which was being used for producing these soft and hard detergents which were obtained from the fatty alcohols. Now the other way of accessing these olefins's are from cracking petroleum large scale cracking of natural oil, natural gas.

So these so there was sort of demand there was sort of demand to go all the way from olefin's to this detergents via this alkyene halide then olefin's and then hydroformlyation and so on so forth this is alkanes. Now at that time the shell chemical discovered shop shell had olefin polymerization process which is called shell higher olefin process. So what is this method this method actually converted ethylene to alpha olefin's not alpha olefin oligomers and not polymers.

And the catalyst used for this is nickel was found to produce olefin polymers from ethylene but the other process was also went on to become a very big industrial hit and won a noble prize and this is Ziegler Natta polymerization if same olefin if it is taken with titanium and aluminum halides then it can make poly olefin polymer. So Ziegler Natta will take olefin all the way to polymer whereas the need was to develop alpha olefin oligomers.

So they are not to high of a molecular weight and that was developed by shell higher olefin process by shell chemicals and this is a industrial process which could would stop the polymerization olefin all the way to polymer and could isolate then in oligomers. So now this was in deed big discovery and then what is important was that these oligomers that were been produced by shell higher olefin had several fragments like it was a mixture of oligomers and then they were at a stake in trying to find out how to utilize all of the fractions of these oligomers.

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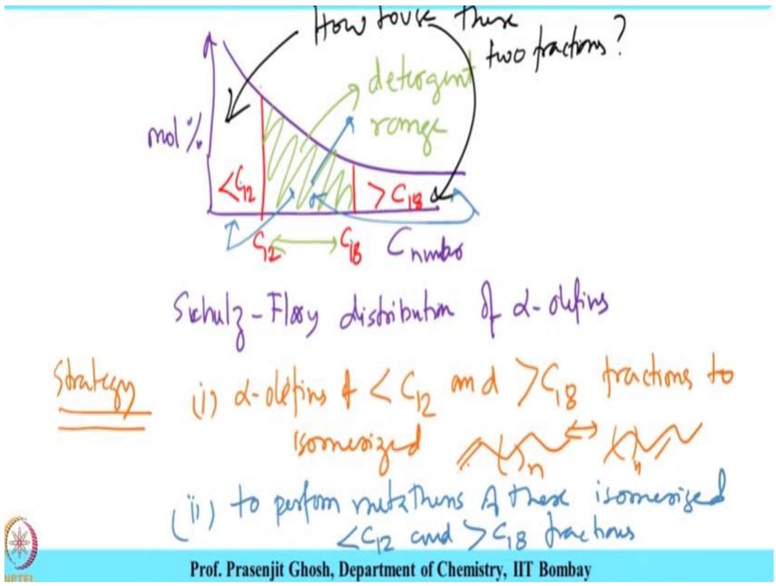

Should best illustrate the point when they were looking at the concentration of alpha olefin produced so this is the mole percent of alpha olefin produced versus carbon number the distribution was like this this is called Schulz Flory distribution of alpha olefin produced from shop process. So what they observed that there is a large amount of alpha olefin's are produced which are lower than C12 fragment this is C12 fragment and there is also large less much number of olefin produced which was above C18 fragment.

Now this was the distribution now what was important over here is that from this distribution only these bottom part from C12 to C14 was of important for detergent range for with then they could make and tap this detergents. So these the middle there was no control for shop process and it could give a lot of alpha olefins which are less than carbon 12 atom and then there would be substantial also which are more than carbon 18 atoms which had no use for detergent purpose.

And the overall focus then was in how to use these 2 fractions and this whole story was developed in shell and what the idea was that this is where they took off took the help of other chemistry. So the strategy was first these alpha olefin's of less than C12 fragments and greater than C18 fragment to be a isomerized fractions to be isomerized that means that for example if there is an alpha olefin it would have somewhere in the middle the olfenic bond getting isomerized with the total number of N being remaining the same.

So some sort of isomerization of the olefinic bond to the isomerization some internal position that is what they looked at. And then the next strategy was metathesis then to perform metathesis of these isomerized less than C12 and greater than C18 fractions. Now the idea is that if these two fractions are done metathesis off then they would give products which would be in these range and again that can be used for detergent purpose.

So this was really a clever way of utilizing olefin's which are supposedly non usable at that point of time and hence the idea was that for them to do isomerization followed by metathesis which will give fragments and in this range of C12 to 18 and then they can further use it for the purpose for which the plant was built.

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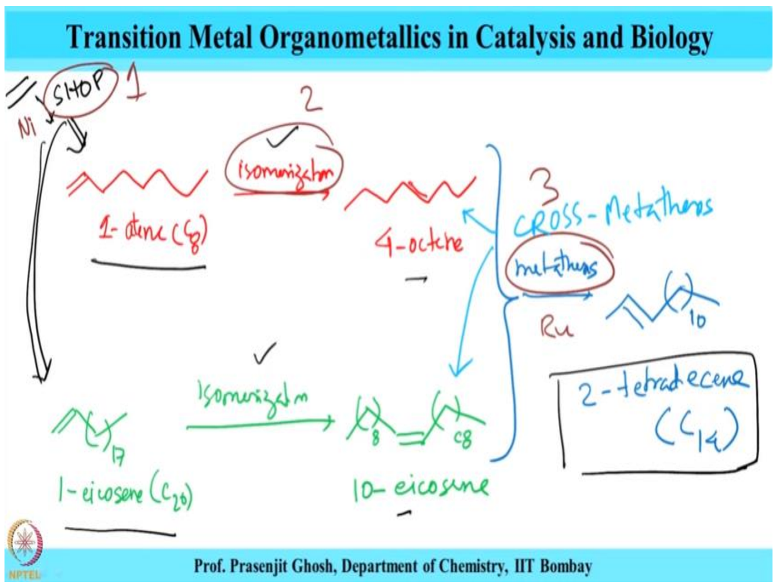

And this is based illustrated in the following slide for 1 octane octane and this is C18 fragment undergoing isomerization to give 4 octane. And similarly CH2 17 this is called 1 eicosene this is C20 fragments undergoing similar isomerization to give C8 this is called 10 eicosene fragment which after isomerization would be subjected to metathesis to give C10 C14 fragment which is called 2tetra disene and this is the D14 fragment.

So what is interesting to note is that in industrial scale by taking the less than C12 and greater than C18 fragment for example 1 octane with C8 and 1 eicoseve with C20 then undergoing isomerization giving this C8 and C20 which would undergo metathesis to give the C14 fragments and these is in the middle for used for making the detergent agent. So this is the very nice way of utilizing in the alpha olefin which were unusable at that point of time.

Now what is important over here to notice that fact that both of these olefin's synthesized from ethylene using shop scale higher olefin process. So now if somebody what shell wanted to do is to apply 3 chemical reactions in industrial scale and the 3 chemical reactions all in a same plant and 3 chemical reactions would thus be. Now this is number 1 then isomerization number 2 and metathesis number 3 all of these should occur without interfering with it any of these and then give a right product and we have seen that the metal used for each of these are different.

For example for the firs step it is nickel whereas for the metathesis step it was ruthenium so there is a lot of optimization that they had to undertake in order to bring compatibility of 3 large scale process is 3 different chemical reaction and then in a industrial scale to be able to produce the fragment they need now these in today's lecture what is important is that these metathesis reaction what they would be carrying out over here is nothing but cross metathesis.

These metathesis reaction is actually cross across metathesis between 2 different olefin's that is exactly what we are seeing it. So this shop process containing cross metathesis is a large scale industrial applications of shop as well as of metathesis chemistry. Now towards this and a lot of research have to taken place there were people expert in shop chemistry developing shop chemistry then people expert in isomerization chemistry as well as people expert in metathesis chemistry wherein put in place to come up with a single flow diagram in which these whole sequences that have gone out here could be realized in an industrial scale.

And that lead to the following flow diagram for the shop production plan which is shown over here.

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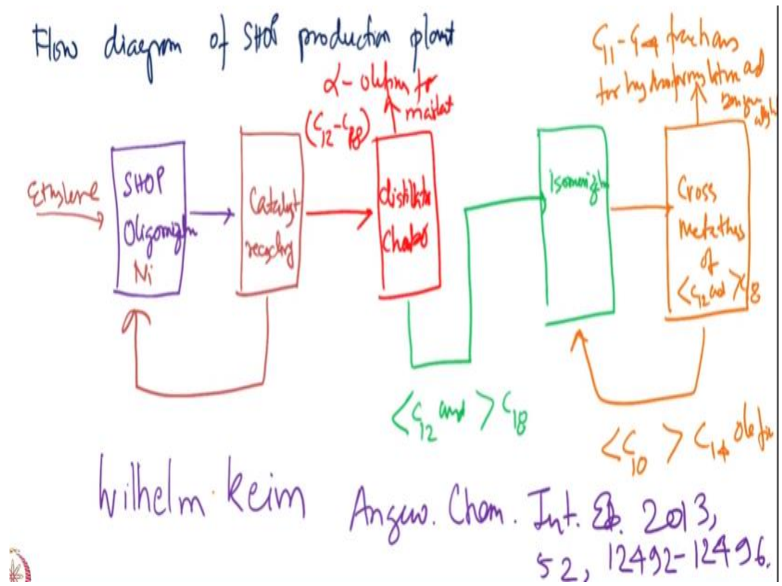

And that given by first ethylene feed so that would enter the oligomerization Jason chamber and then that would lead to the second chamber which would be used for catalyst recycling. So the Nickel catalyst used for shop would be recycled back for next phase then comes the distillation chamber which will give alpha olefin’s for market and these would be C12 to C20 fraction C18 C12 to C18 fractions.

They would be straight away used from market and then the remaining fractions which are less than C12 and greater than C18 would be taken to the fourth chamber which will involve isomerization. And then post isomerization next what remains is cross metathesis and this would off less than C12 greater than C18 fractions. And then finally the product would be C11 to C14 fractions for hydroformlyzation and benzene alkylation.

So the next formats would be used for that and the remaining the smaller one would again be recycled which is less than C10 and greater than C14 olefin’s. So these is a nice demonstration how the need for detergents or the need for detergents grade alpha olefin’s late to development of 3 important major industrial reaction all being carried out in a plant and this was developed by shell chemical and nice article about these perspective development has been given by Wilhelm Keim who had been witnessed to this development of shop from their industrial research to that to the industry when he was working at shell chemical and as given a nice account in Angew chem international edition 2013,52, 12492 to 12496.

So with these I come to the conclusion of today’s lecture which was on cross metathesis particularly with regard to the applications of cross metathesis and in this prospective we have taken up the whole developmental story of cross metathesis reaction with respect to shell higher olefin process which was developed at shell chemical and the whole perspective given from professor Wilhelm Keim in the perspective given in Angew chem international edition 2013 volume 52 12492 to 12496.

This is excellent read I suggest all the student of this class to refer to this article and to see how need as lead to interesting development and here it was one which was done at industry where 3 big reaction were put in place for large scale production to arrive at the need of what they wanted which was about see for mid-range alpha olefin’s. So with these I conclude today’s lecture and I look forward to discussing more on various application aspects of cross metathesis reaction when I meet next till then thank you and goodbye.