Transition Metal Organometallics in Catalysis and Biology
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Module No # 02
Lecture No # 06
Metallative and Conventional Reppeand Metathesis Reaction (Introduction)

Welcome to this lecture on transition metal organometallics in catalysis and biology today we are going to be discussing 2 important topics. First we are going to be finishing off our discussion on Reppe synthesis an important acetylene chemistry which was developed in early 1900's also. And then which even have a relevance in today's context and then go on to another important topic which is metathesis reaction which also had been very interesting area of chemistry and had been recognized by the conformant of Nobel prize as recent as 2005.

So continuing with our discussion on Reppe synthesis we would like to talk about the type of reaction that we have covered in the Reppe synthesis. What we had seen that Reppe synthesis sort of (()) (01:24) are 4 different types of reaction all staring from a very simplest see to feed stock which is as a clean and conversion of acetylene to different Vinyl derivatives like Vinyl alcohol Vinyl cyanide, Vinyl chloride this is one step convergent of acetylene and this type of reactions are called Vinylzation reaction then we had also seen the reaction of acetylene with aldehydes where it is just alkyne analyzation reaction where it is just acetylenic just add against the CO bond.

We have also seen the reaction of acetylenes with carbon monoxide water and these are hydro carboxylation reaction and all of these what we had seen that they produce functionalize acetylenic aliphatic feed stocks which are very important for various transformation in chemical industry. In the last lecture we had talked about cyclo oligomerization reaction.

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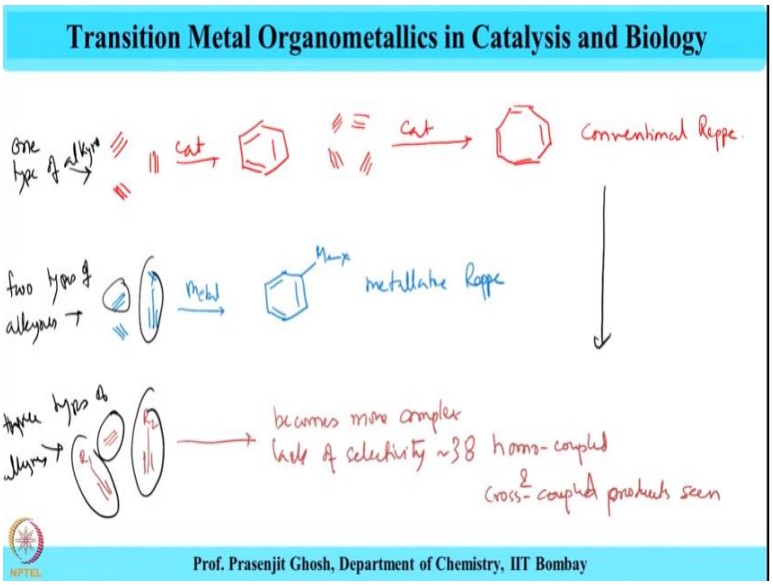

Particularly in terms of with regard to making aromatic compounds using Reppe. So for example the reactions of 3 acetylenic fragments giving benzene is an interesting example of this conventional Reppe reaction. Or proceeding further we have looked into the reaction of 4 cyclo tetramerization of acetylene giving cyclo octatetra in and these are nothing but conventional Reppe.

Now in past lecture we have also looked at the formation of methylated Reppe where 2 different kinds of alkynes are used in presence of a metal and these are called metallive Reppe. Now what one can see that in this case one type of alkyne is used and in this case 2 types are alkynes are used. Now when one develops the compound further for example in cases where 3 different kinds of alkynes are used then things become more complex like lack of selectivity about 38 cross homo coupled and cross coupled product are obtained.

So the things becoming different when there are 3 different kinds of alkynes so here as we go from here let me see that this expansion of Reppe chemistry with regards to formation of different kinds of aromatic compounds by combination of single acetylene single type of acetylene to 2 types of acetylene what happens when are 3 different types of acetylene have been used.

Now to tell that this Reppe chemistry is relevant even today is this fact that in this century in 2001 this problem of 3 different acetylene has been to give a very selective product have been

nicely demonstrated in this particular paper of journal of chemical society 2001 123 7925 to 7926.

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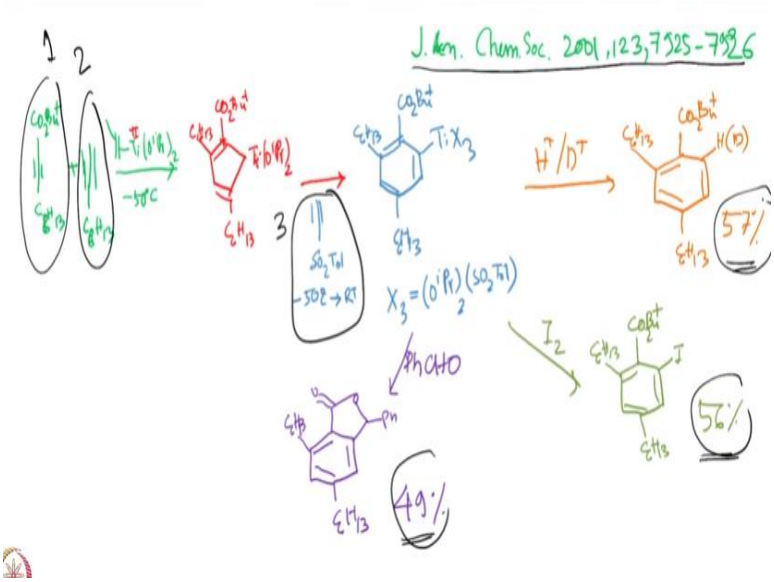

So here the metallative Reppe with 3 different acetylene's to give highly selective products as been successfully demonstrated and we are going to see how this is done this as been done. One thing for to note here that these conversion these reactions of 3 different acetylene has not been done together all at once but as been done in a step wise fashion as we will see in the synthesis.

The synthesis starts with C8H13 this is acetylene number 1 with another acetylene oh this is C6H13 reacting with a titanium catalyst titanium propene catalyst so is interesting catalyst at -50 degree centigrade where the titanium is in class 2 state to give this cyclo methylated species H13 as appear to. So here that reacts with acetylene at -50 degree centigrade and then the reaction is at room temperature to give this aromatic 6 membered ring with CO2 butane C6 H13 DIX3 where X3 equals OIP at 2 SO2 Tol.

So these when treated with H+ or D + methylate's the ring giving the product C6H13 HD and this happens in 57% this when treated with iodine gives this iodide derivative in 56% in and this when treated with benzaldehyde gives C6H13 this bicyclic compound in 49%. So important message over here is that this difficultly in attending selectivity in Reppe synthesis was overcome in this beautiful work published in journal of American chemical society 2001 volume 123 7925 to 7926 communication paper where the 3 acetylene.

Acetylene's 1 and 2 and the third one have been used sequentially to produce this aromatic ring and good thing is that they have been produced in highly selective fashions in very high yields. These is different from earlier challenges that was involved associated with Reppe's synthesis with regard to trying 2 different alkene's to form these aromatic compounds. And a nice demonstration these can be seen in this recent paper 2001 paper where one can see that high selective product was synthesized using methylated Reppe using 3 different alkynes and all under methylative Reppe conditions.

And another thing to note is that this recent work was published was recently as in 2001 which is about 70 or 80 year earlier then when the Reppe chemistry was really invoked. So what it says and finds out is that indeed Reppe chemistry is very relevant in today's context and there are quite a big amount of interest that is still there in the developmental reaction and some very (()) (16:09) studies have emerged from Reppe chemistry.

So with this I am would like to end our discussion on Reppe synthesis and to give your feel for different Reppe products one can observe let me just summarize the various kinds of products that we had observed and seen from Reppe reaction.

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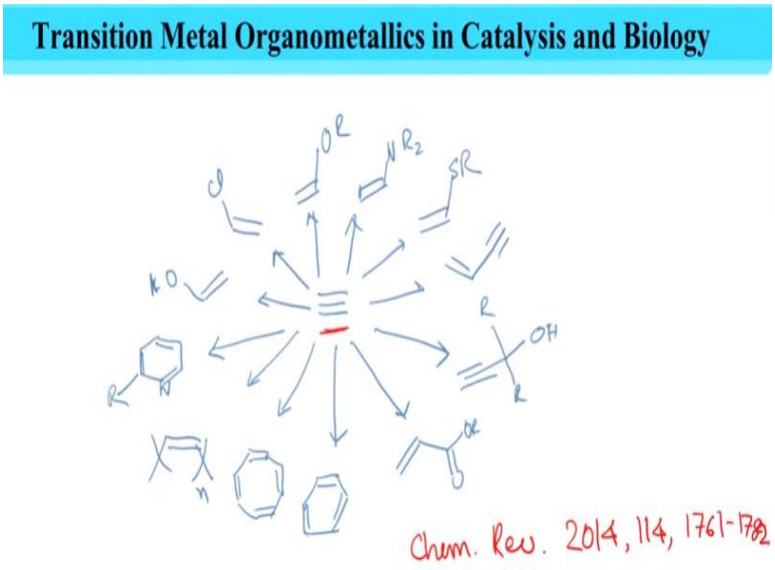

So we had seen formation of (()) (17:02), formation of acetates anides tayos, alcohols (()) (18:01) benzene's, Cyclo octatetreane even they can be converted to various kinds of polymers and kind

also be converted to different period in derivatives. So these gives flair of how which the Reppe chemistry is in terms of different products it produces and in short this slide sort of summarizes a different form of Reppe product tells the strength of Reppe chemistry in terms of producing so many different compounds from a very single studying source.

So this s why the Reppe chemistry is so important and more on this can be seen in this chemical review which I had given reference on if somebody wants to look up can study the same and find more facts about it. So with these we are going to stop our discussion on reppe chemistry and we are going to be taking up another important topic which is olefin metathesis. Olefin metathesis is a very interesting reaction this is a important reaction and consider as a milestone in polymer in development of polymer chemistry.

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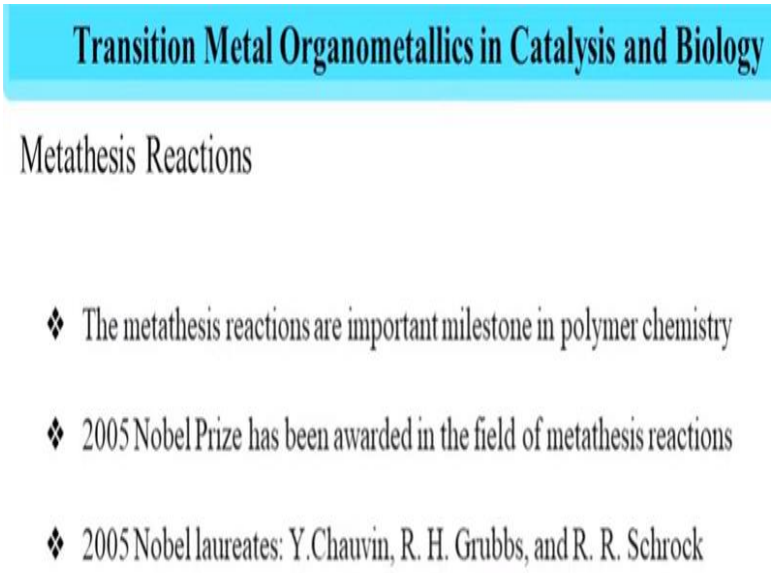

If you look at the in terms of development you know the metathesis polymerization sort of came slight even though it originated around at the time of olefin polymerization ply olefin synthesis. However the recognition in terms of is impact to the society came much later about 50 or more odd years later and as 2005 when it was awarded the noble prize. And this Nobel prize for metathesis reaction were awarded to 2 distinguished chemist professor JL Chauvin, Professor Robert H Grubbs and Professor Richard R Schrock for their development or for their contribution in metathesis reaction.

Now unlike previous topic where which we have covered where Reppe chemistry he has been contribution from the industry more then the academic work the metathesis reaction had been evolved in the laboratories of academic as well as industry and probably much more in academic work than in the industry with many contributing from the world of academia. Professor Robert Grubbs is from Caltech professor Richard Schrock is from MIT and professor Chauvin form France.

So we have here we see that 3 professors 2 from US and 1 from France being awarded recognized their contribution in metathesis. One thing this at this (()) (22:22) I must note that even though that these 3 professors were formally recognized for their contribution in metathesis. Metathesis as a field evolved with lot of players and lot of interesting minds contributing on working on it even though 3 of them were finally organized for their contribution.

Now the metathesis as mentioned had been chained up in this industry to being with because there were lot of unexplained unusual observation that were seen in the chemical industry when it was first observed. So what is important over here is that as I said that both olefin polymerization as well as olefin metathesis.

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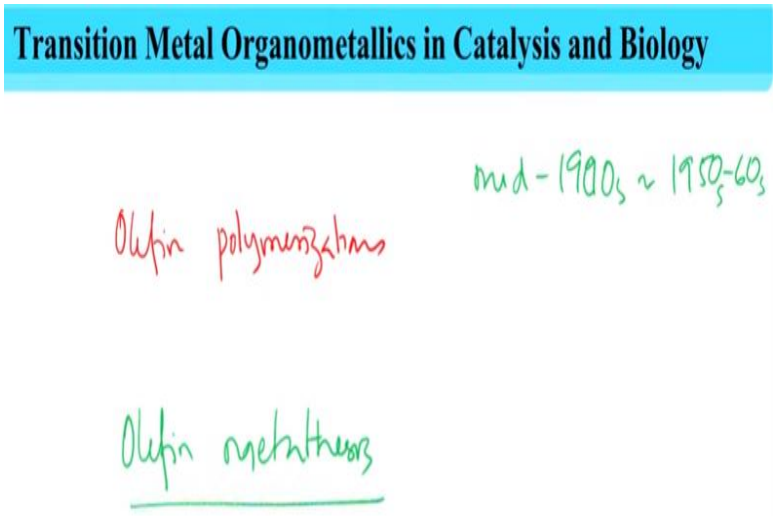

Olefin metathesis were of interest in mid 1900, 1950, 1960's it is the olefin polymerization which was sort of tracked much earlier or it will found understood where I understood much earlier simple coordination insertion polymerization then olefin metathesis. So much of the time

in metathesis was lost in trying to understand the phenomenon of metathesis and that is why the field of metathesis sort of was developed about 10 or 15 or 20 years later and then the field of olefin polymerization.

In my opinion earlier breakthrough in terms of understanding and mechanism then olefin metathesis even though both probably where of interest or where been explode at in the similar around the same time but one just got the understood better and earlier than the other. So with these I conclude today's lecture where we have looked into this Reppe synthesis particularly with it we get to cyclo oligomerization of acetylene to produce aromatic compound using (()) (25:21).

And what we have discussed in today's lecture is about the use of 2 different alkyne's to form aromatic compounds with highly substituted aromatic compounds with high selectivity because the one of the challenges had Philip had been on going from 1 type to 2 type or 3 type of different alkyne's is that there was drastic loss of selectivity with about 30 odd over 30 odd (()) (25:58) cross couple products being formed simultaneous formed in this process.

So we had seen that in a beautiful work as let as early as 2001 about 50, 60 years since the discovery of Reppe is that this has been solved very elegantly using 3 different acetylene's to produce selective aromatic products using a titanium catalyst yet it covered that. In this lecture we have also looked into different kind of products that Reppe chemistry throws out and shows that it makes a large amount of product which completes the whole cycle.

So the utility of Reppe chemistry still stands today and with that we have also completed concluded our discussion on Reppe and we had initiated our discussion of olefin and metathesis another very interesting Nobel prize award winning reaction with regard to olefin metathesis what we have spoken about is that even though olefin metathesis an olefin polymerization probably were of interest around the same time which is around mid 1900, 1950's, 40's, 60's.

It is the olefin polymerization which was understood much earlier and his (()) (27:22) will and recognize much earlier with Nobel prize in 1953 or 63 whereas for olefin metathesis the puzzle remained for another 2 or 3 decades because before people could understand what is going on in this new and which diverse chemistry and then finally the impact that it was felt slightly few decades later with the Noble Prize awarded in 2005 about 50 years after.

Then that of olefin polymerization so metathesis also is important breakthrough in the field of polymerization you know we would also look into various aspect of olefin metathesis have in the subsequent lectures what is important to say is unlike Reppe chemistry which had been exclusively or have been solely developed in the purview of industry metathesis development had been largely a both in academic as well as in industrial work even through 3 person who have been recognized finally recognized and given awarded the real prize belong to this academic world 2 from US and another from France.

So with this I conclude today's lecture we going to be taking discussing lot on olefin metathesis when we take up the next lecture so I thank you once again for being with me in the existing journey of different applications of transition metal organometallics in chemical catalysis. And I look forward to being with you in the next lecture where we are going to be talking about olefin metathesis in much more detail and depth till then good bye and thank you.