

Transition Metal Organometallics in Catalysis and Biology
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Module No # 01

Lecture No # 05

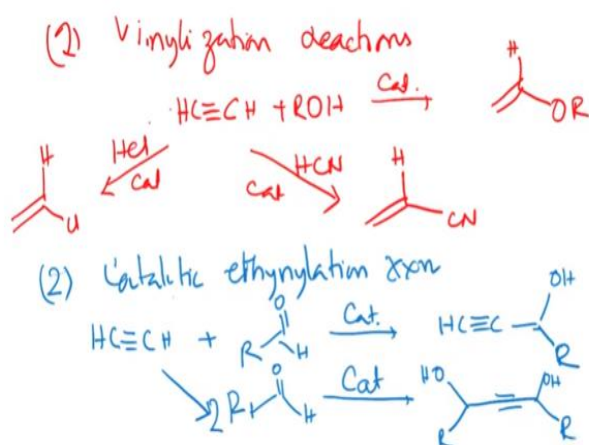
Metallative and Conventional Reppe and Metathesis Reaction (Introduction)

Welcome to this course on transition metal organometallics in catalysis and biology we have been discussing a very important reaction in the context of application of transition metal organometallics in catalysis and this is about this Reppe chemistry or Reppe reaction which have been developed by Walter Reppe in early 1900 and this has been an effort which has been absolutely a developed in industry and had been great contribution to the reach chemistry of transition metal organometallics catalysis that is been seen today.

Now in this context in the earlier class we have looked into various kinds of Reppe reactions and to this extent we have covered nearly 3 types of Reppe reaction starting with Vinylization reactions.

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Transition Metal Organometallics in Catalysis and Biology



And examples of this giving vinyl cyanide's as well as with HCl and catalyst giving vinyl chlorides. The second reaction that we had covered is this catalytic ethynylation reaction and in this we have looked into reactions of aldehydes giving alcohols of kind shown as well as the same with 2 equivalents in presence of catalyst giving diols of the type. The once drawn over

here and we have also seen the reaction with carbon monoxide and acid giving acrylic acid and acrylates.

Now we have discussed these 3 reactions or type of reactions in great details and when we have observed that these reactions all required intervention of catalysts and precedes via formation of organometallic species and the catalyst used often involved Nickel, Copper, mercury and iron, ruthenium so on and hence so forth in getting the kind of chemistry that have been detailed over here.

Now I must also mention that these products are useful as monomers are important monomers were various polymerization reactions and hence they are sought after very much in industry. Now in this context another very important reaction which comes into play which is developed by Reppe and this involves the formation of vinyl pyrrolidone synthesis. This is a reaction which is important from industrial point of view and the sequence is shown is over calcium carbide in presence of catalyst gives an acetylene.

That presence of formaldehyde catalyst and 300 to 350 psi gives this diol which we had just discussed about that upon reduction and complete reduction gives the 1,4 diol and using (1,4) (07:25) that we had also discussed about and these then undergo dehydrogenation to give this cyclic lactile which upon reaction with ammonia at 230 degree centigrade gives the cyclic amine and that when further reacts with acetylene at 150 degree centigrade gives vinyl pyrrolidone.

So these is an important outcome of Reppe synthesis which was formally patented by Reppe and was a big draw of from outcome of different product which had come up the review synthesis in the sense the simple acetylene compound was converted to this pyrrolidone moiety using Reppe chemistry. So this shows that how a very complex molecule which is also important feed stock in chemical industry can be synthesis using convergence of acetylene using Reppe chemistry.

So this was one of the big draw of Reppe chemistry in overall and there was a patent which had come out of it.

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Transition Metal Organometallics in Catalysis and Biology



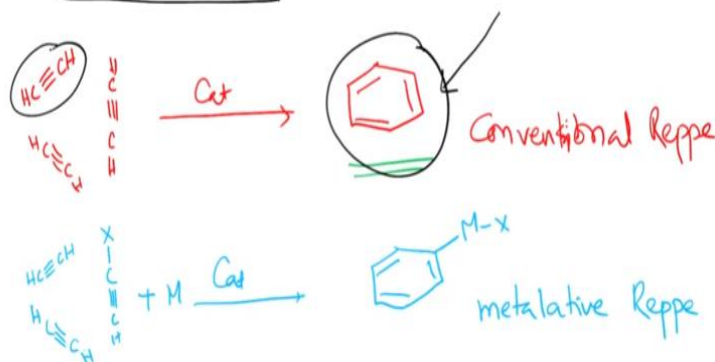
Reppe explaining the synthesis of polyvinyl pyrrolidone

And here is a picture showing Reppe explaining the synthesis of polyvinyl pyrrolidone leading on the board. Now with these we come to an very important aspect of Reppe chemistry which involves cyclo polymerization reactions or cyclo oligomerization reactions using mediation of metal.

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Transition Metal Organometallics in Catalysis and Biology

(F) Cyclo-oligomerization rxns of $\text{HC}\equiv\text{CH}$

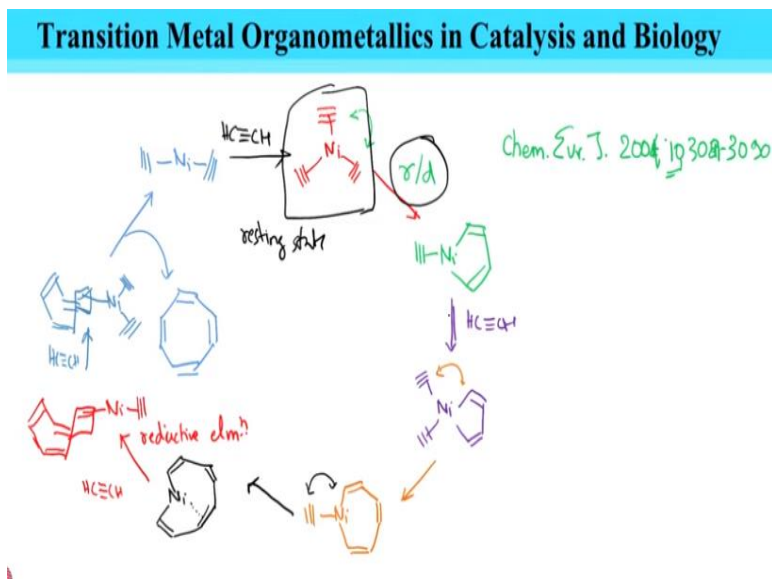


So cyclo oligomerization reactions of acetylene these are the fourth type of reaction that the Reppe chemistry shows. The for example and this also proceeds the mediation of the metal the first of it is shown over here that with a catalyst give benzene and these are called conventional Reppe reaction. The beauty of this synthesis can be seen that aromatic compounds can be obtained from acetylene moiety.

And there is a different kind of Reppe reactions which are called methylated Reppe which is shown over here where involves 2 different kinds of acetylenes. So this requires metal catalyst and it also gives a aromatic compound with metallic bond which can further be functionalized and these are called metallative Reppe. So what we see in this today's lecture that there is a very important dimension to Reppe chemistry where not only simple functionalized acetylenic products in terms of vinylization, ethylenization as well as hydro carboxylation moiety into simple aliphatic compounds.

Not only can they be formed but Reppe reaction can be extended more conveniently to produce more complex and intriguing aromatic compounds. So in the next few minutes we are going to focus on different kind of Reppe cyclo oligomerization reaction and to begin with we are going to look at the formation of the benzene from acetylenic fragment in a conventional Reppe system. That the formation of the Reppe from this acetylenic system is based elaborated by an active species which is formed from acetylene adduct of nickel.

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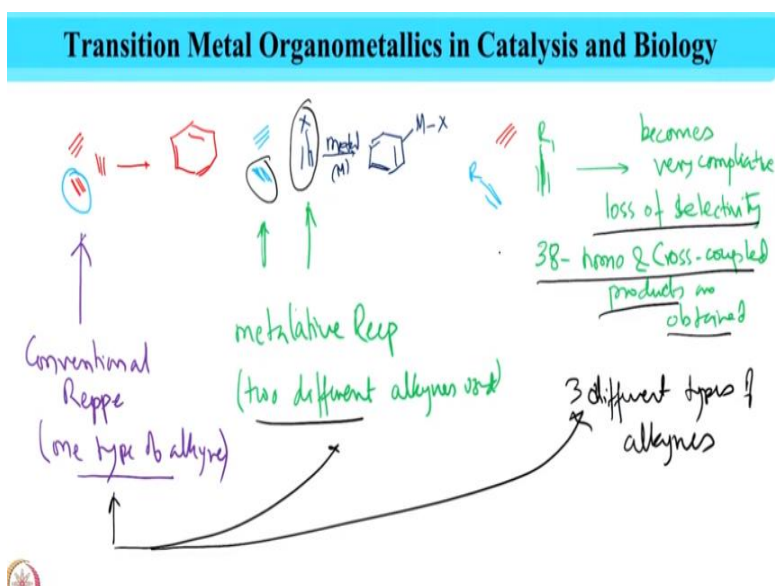
So is what is suggested that nickel cryogenic species is found initially as a catalyst which is the active species for this Reppe cyclo oligomerization and then once this species is formed it undergoes this cyclization reaction between these 2 acetylene to give acetylene bound nickel cyclo methylated species. And this has been extensively probed using dft in a paper which elaborates the path way where it says that this is the rate determining step for the reaction.

Now the different for this study is given in this journal chemistry European journal 2004 volume 10 3081 to 8123090. So one can look up this study in bit more detail if one were interested in and see how this cyclo oligomerization proceeds. Now once this is formed that reacts with another acetylene moiety to give this nickel this acetylene cyclomated species which then undergoes another insertion of the acetylene to give a 7 member ring and that then further undergoes insertion of this acetylene to give this species which is a nickel bound 9 member species of the type shown over here.

And once this is formed in presence of another acetylene this species undergoes reduction elimination to give the corresponding cyclo octatetraene bound nickel acetylene species. Now these in presence of acetylene gives the nickel this acetylenic species and which eventually which eventually loses this cyclo octatetraene to give the nickel miss acetylenic species and that finally in presence of acetylene comes back to give the these acetylene active species.

So this is the resting state of the catalyst and this is formed in this cyclo pathway so this is an interesting reaction and what it seems that the first step of formation of this cyclo methylated cyclopentane metallocyclopentane type complex is the way determining step of such cyclo oligomerization reaction. Now proceeding further another interesting thing about these Reppe chemistry is that when these cyclo oligomerization reactions are performed the reactions sort of works well for symmetrical for works will same or singular substrate for the same substrate.

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For example over here the oligomerization happened using same type of acetylene so the Reppe reaction sort of works very good for cyclization of similar kind of acetylene for example these going to these. So there is only a 1 type of acetylene being used or for the reaction giving in presence of metal catalyst M where 2 different kinds of acetylene one is this other is this kinds of acetylene produce but when sort of one goes to use 3 different kinds of acetylenes.

For example then things becomes complicated becomes very complicated in terms of loss of selectivity and 48 different coupled products 38 cost homo and cross coupled product are obtained. So these is an inherent difficulty in Reppe synthesis so what we are discussed are seen today is that there is Reppe chemistry as a dimension which is unique and very interesting in terms of being able to use acetylene fragments towards the formation of aromatic compounds and these is very different from simple vinylization reaction or ethylenization reactions or even the reaction with carbon monoxide.

Where the functionalization of acetylene to various important small molecule functionalized elliptic feed stocks where synthesized whereas by the fourth reaction that we had discussed today cyclo oligomerization of acetylene to give aromatic compounds starting from benzene or cyclo octatetraene what we have found this indeed is a very interesting aspect of Reppe chemistry where the cyclo oligomerization has happened.

Now what we have discussed to today's class with regard to cyclo oligomerization we have looked into the reaction of cyclo trimerization of acetylene to give cyclo octatetraene and what we had seen that the formation of matrix acetylenic nickel 0 species is the active species which is responsible for the catalysis. And what we would also seen in the formation of a 5 membered metallocyclopentane ring in that catalytic cycle is the rate determining step for these.

We have also looked into metallative Reppe which involve again the formation of aromatic compound but in this case there are 2 different kind of acetylene which are used in metallative Reppe this is metallative Reppe where 2 different alkynes used. Whereas in conventional Reppe this is conventional Reppe of 1 type of alkyne and then we also discussed that as we move from 1 type alkyne to 2 different type of alkyne to even 3 types of alkynes.

Then the game become even more difficult with loss of selectivity and a large number of homo and cross coupled products are observed and then the system for the cyclization of these 3 different kind of becomes very challenging. Now we are going to take up these in bit more detail as how this was solved in nice demonstration of fine organometallic chemistry where even the Reppe coupling of 3 different alkynes to give highly selective aromatic products could be obtained and this would be taken up in the next class.

So with these I come to an end today's discussion where we had looked into a very interesting aspect of Reppe chemistry which are cyclo oligomerization of Reppe from alkyne producing aromatic compound and in that we have discussed about the formation of conventional Reppe where only 1 type of alkyne is used or even the methylated Reppe 2 different kinds of alkynes are used.

We have also looked at mechanistic pathway in which the conventional Reppe towards cyclo tetramerization of alkyne to cyclo octatetraene was obtained using a nickel catalyst and with this I conclude today's lecture and in the next lecture we are going to be discussing more about using 3 different kinds of alkynes even in the context of Reppe chemistry to produce highly selective aromatic compounds which are indeed challenge for Reppe synthesis. So with these I conclude today's lecture and I look forward to be seeing you in the next lecture where we take up this interesting ocean of Reppe chemistry till then good bye and thank you.