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**NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING**

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**Organometallic**
**Chemistry-I**
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**Module No. 5**

**Lecture No. 20**

# CARBONYLATION REACTIONS
## 1. HYDRFORMYLATION
## 2. HYDROCARBOXYLATION
## 3. HYDROCYANATION

Welcome back in the last class we were mainly focusing on the Monsanto acetic acid process of the carbon lesson and then we have seen the hydroformylation reaction now in the today's class we will just briefly discuss one of the asymmetry car equivalent asymmetric case of the hydroformylation reaction and then we will try to discuss the hydrocarboxylation and if time permits we will discuss the hydrocynation reaction hydrocynation and reason as you know by default it is not really carbon reaction but you know hydrocynation is similar to that of the carbon lesson mechanism.

So we may want to put that in the similar bracket okay so today again will mainly focus on one of the symmetric case and then I hydrocarboxylation asymmetric, asymmetrichy hydroformylation is the one we will discuss on the beginning okay.

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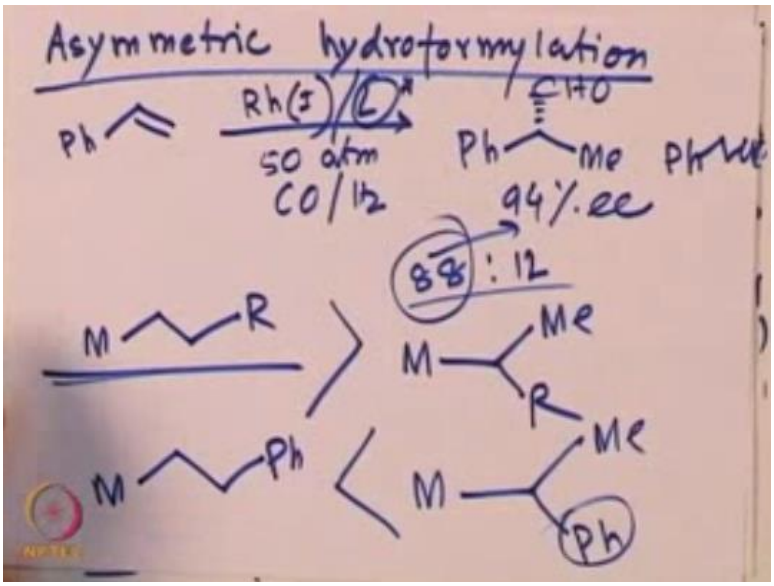


Asymmetric hydroformylation reaction are very, very important reaction and again these are the reaction industrially done in a huge scale assymmetric hydroformylation reactions one of the component could be of course if it is a linear product as you know as you have seen in the last class there is no chance of getting any a symmetric one right especially if it is the terminal olefin and linear one we are not going to get it but if it is a styrene one or a branch product formation is happening.

Then we can have this ligand which is chiral and then we can have an opportunity to get the product in asymmetric fashion let us say for this case with a suitable ligand this gives the branch product and ee is greater than greater 94% and that means that of course 88 is to 12 ratio of a of the of these this product right it a 88 to 12 ratio for this linear is to brand product okay now effort for this particular case that is very good and we have 94 % ee for these reactions and we of course have the linear product little bit.

So come from this styrene equivalent we have two product formation and that is the linear product that is Ph CH 2 CH 2 CH 0 and the branch product and if we are having a suitable ligand which is asymmetric in nature which has suitable chirality we able to get the brunt product in

enantiomeric excess that means in asymmetric person and we are we are going to get for this particular case let us say we get a more than 90% ee that which is considered to be very good and 95% ee that is considered that is really very good and then of course we have a linear is to brand product formation 12 is to 88 ratio that is again quite a good achievement but one must notice.

Why these are brand product is all of a sudden is the major product why not the linear product is a major product that is what we need to understand one must understand that this is styrene this is not propane or other aliphatic olefin and therefore the answer lies within the nature of the olefin let me let me draw the metal alkyl species so for the metal alkyl species if it is a aliphatic one this is the one which is going to be the more stable and the primary one and the secondary one is the one which will give you the brand product, okay.

It is going to be less stable that is why for propane for example the one which we were discussing in the last class this linear product is the major one the brand product is the minor one. But for styrene what is happening that this is the metal alkyl this is the least favored and this branch to one or the secondary alkyl species is more stable because of the charge distribution or the or the stability of the intermediate due to the resonance with the phenyl ring okay negative charge is stabilized by phenyl ring and that is how we have seen that this product formation is going on.

Indeed this is how the naproxen which is the NSA non-steroidal anti-inflammatory drug which is used for pain and pain fever inflammation and stiffness are also for kidney stone that naproxen which is actually a very well will sold drug and it is synthesized by name or tolyl by nap a by nap or tolyl by map and this is a naproxen is synthesized in a symmetric axon by utilizing this technique, okay.

So what we would like to take the message is very simply the asymmetric person of hydroformylation reactions are widely used in the industry specifically a lot of drug molecules can be synthesized one of the most important example as we try to say is the naproxen synthesis which has which has the naphthalene unit instead of the benzene ring this is synthesized in large scale with a by nap or tolyl by map as the ligand in industrial scale.

And we know that this naproxen is a one of the best-selling perhaps drug in the world and it is used for it is actually in acid, so that means non-steroidal anti-inflammatory drug and it is used quite large scale all over the world, okay. So all these reactions simple reactions but can be utilized for humankind for industrial scale and therefore we do want to understand the mechanism of it and we have just seen that these mechanisms are very simple.

And that it is consisting of the fundamental steps that we have discussed so far in the class, in the next part we would like to discuss the hydrocarboxylation reaction the mechanism and as you will see this is again one of the simplest reaction and quite huge full in industrial setup let us try to look back at that.

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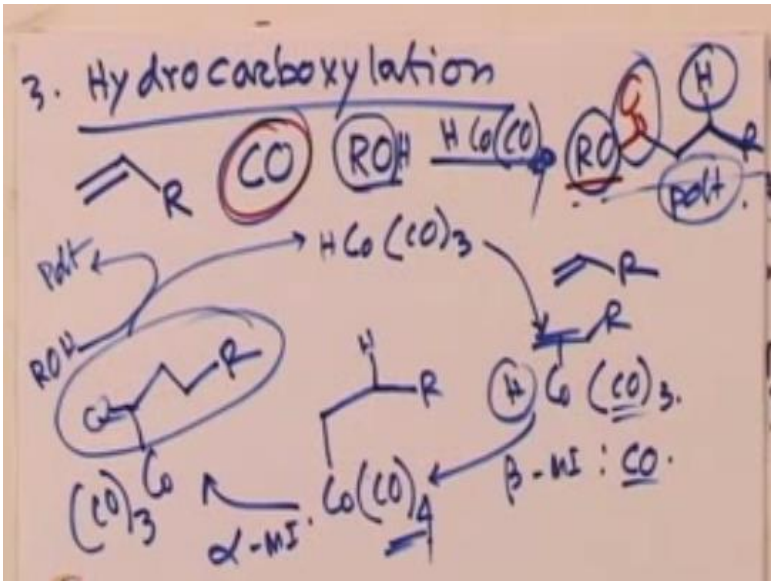


Hydrocarboxylation reactions, okay. Now for this reaction we again have an olefin carbon monoxide and alcohol, okay we have the we have the same catalyst cobalt catalyst tetra carbonyl and we have the product formation where this is the R0 equivalent this is the R0 and then we have the CO that is the CO, okay. And then our only fine equivalent with two of the hide with the hydride in there too, right.

So we have RO okay from this alcohol we have carbon monoxide from here and we have R molecule equivalent from there, okay. Now of course this reaction is going to be similar as you can perhaps now draw the mechanism of it, okay, I expect perhaps you should be able to do by now it is a stepwise mechanism if you try to draw I think there is a good chance that you will be correct in predicting the mechanism let us anyway let us try to try to draw the mechanism over here and that will be the kind of the final mechanism for this course and of course perhaps we will not be able to discuss too much on the hydrogenation reaction the mechanism will be exactly similar what we have seen so far. Let us try to focus on the hydrocarbons lesson reactions.

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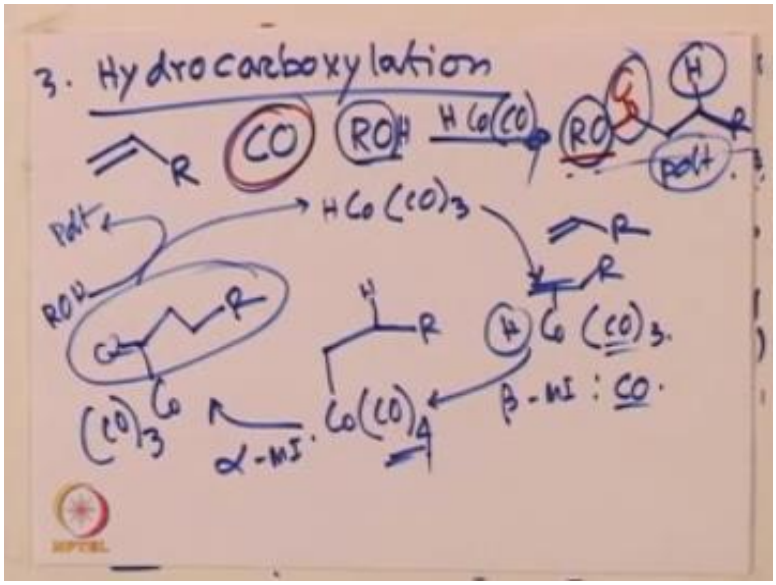


So we start with start with this CO(CO)3 equivalent of course one of the CO unit will be lost that is the first step as you have seen in the last case and starting from there olefin we will coordinate therefore you will have olefin coordinated cobalt intermediate from there on a beta migratory insertion will occur and the carbon monoxide will also come in we are kind of let us say in a little bit and therefore we have beta migratory insertion of this hydride into the olefin you get the alkali metal alkyl species.

And of course also carbon monoxide getting so three carbon will become for carbonyl from there on alpha migratory insertion occurs to give you the intermediate where one of these four carbonyl gets into the or alkyl group migrates into one of these four carbonyl unit and then you get this equivalent which is ready for now. The alcohol to give you the product okay, so the alcohol comes in and you get this product formation, so this is the product right.

So again once again this is very, very simple the mechanism wise I guess you know the simplest hopefully by now to you we have seen the metal carbonyl species hydride metal carbonyl species losing one of the carbonyl first interacting with the olefin and therefore beta migratory insertion and CO coordinates and gives you the metal alkyl intermediate from there on alpha migratory insertion these steps are going to be repeated, right.

Exactly same thing we have simply before the same thing is following but only thing in the last step for the hydroformylation you have seen the hydrogen gas coming into the picture we have discussed that it is not perhaps not the oxidative addition of the hydrogen gas most likely it is a σ bond metathesis in this case alcohol comes into the picture and then from that SL intermediate we have alkyl carbonyl intermediate we have effect by the alcohol to give you the product, okay.

We will look at that last step once again just like the hydroformylation case we have looked at the hydrogen gas addition to the metal carbon alkyl carbonyl intermediate here also we will look at that alcohol intermediate how these are is attacking on the metal carbonyl intermediate, okay alkyl carbonyl intermediate which is bound with the metal, okay. Let us try to look at that so the mechanism one.

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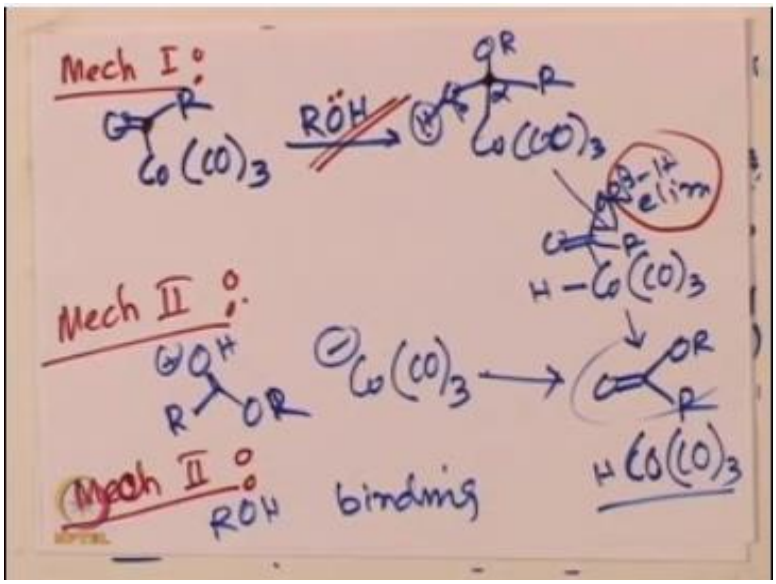


First mechanism for that step we need to draw the last step or last molecule what we were discussing so this is the twist carbonyl cobalt intermediate with COR equivalent in there if you have alcohol, of course alcohol can directly attack at this carbonyl center gives rise to the intermediate where I drop so from this one will be coming and OR it is a tetrahedral intermediate and from thereon you have β hydride elimination this is α this is β α β hydride elimination so β hydride elimination can give you HCO $CO_3$ three equivalent along with the coordination of this $CO_R$ OR equivalent.

Right $CO_R$ or equivalent from there you will get your product formation that you are looking for OR and R right village of this so what you have seen so far is that alcohol is attacking at this carbonyl center giving rise to the tetrahedral intermediate where you have α β position hydride this β hydride elimination can give you give you the product formation along with the cobalt hydrido intermediate back to the to the method.

Another mechanism would be mechanism to second mechanism where you will generate upon attacked by this equivalent by this alcohol you will you will generate just like $SN_2$ reaction you will generate ROH + and OR and this CO - will be generated right so OR and this is the this is

this carbon ionic intermediate will be generated and from there once again you will get the get the equivalent of this product formation where cobalt and the corresponding product is getting generated so these are the two step of course another could be another could be mechanism make there could be another mechanism.

Where the methanol make mechanism three where these alcohol will coordinate with the metal center arrow H will bind to the metal centre and give you the corresponding product formation so in the last step what we have seen so far of these hydrocarbons elation reactions there are three different possibilities one as the last one the third mechanism could be ROH is binding with the metal centre and then therefore attacking to the alkyl carbonyl equivalent that is the third mechanism the first mechanism.

We have seen that ROH is attacking on the carbonyl centre and giving rise to the tetrahedral intermediate from where the hydride elimination is occurring to give you the product formation the second mechanism which is basically direct attack and you know in a concerted mechanism where you attack and release the metal equivalent from the intermediate right so all these three mechanisms are possible it is you know it is still under debate which was exactly which is the one that is exactly going on in these cases okay.

So for the hydrocarbons elation reaction we have seen the similar mechanism to that of the hydroformylation reaction of course both the hydroformylation and hydrocarbons unless and reactions we have seen that there is some ambiguity in the last step which is of course one of the most crucial step we have discussed about the hydroformylation in the last class in this class we have seen the hydrocarbons lesson reaction and plausible three mechanisms are thereof course still it is kind of void open which mechanism is predominant or which mechanism occurs in these cases now of course as you can understand the there would be an opportunity to do the do the hydro carbonization reaction in an isometric fashion.

Similar to that hydroformylation reaction if you have styling or let us say vinyl naphthalene or other royal group as the part of the olefin or the you know denial then gene or denia land I will molecule if you are having then once again similar to your hydroformylation reaction you will

get the brand product formation and if you have the suitable ligand for the metal center you can induced reality into the molecule so a cemetery version of this reaction can be developed by shoe having suitable ligand okay, with for the integration of time will briefly discuss again the hydrocyanation reaction I think we can discuss it for next 5 10 minutes or so.

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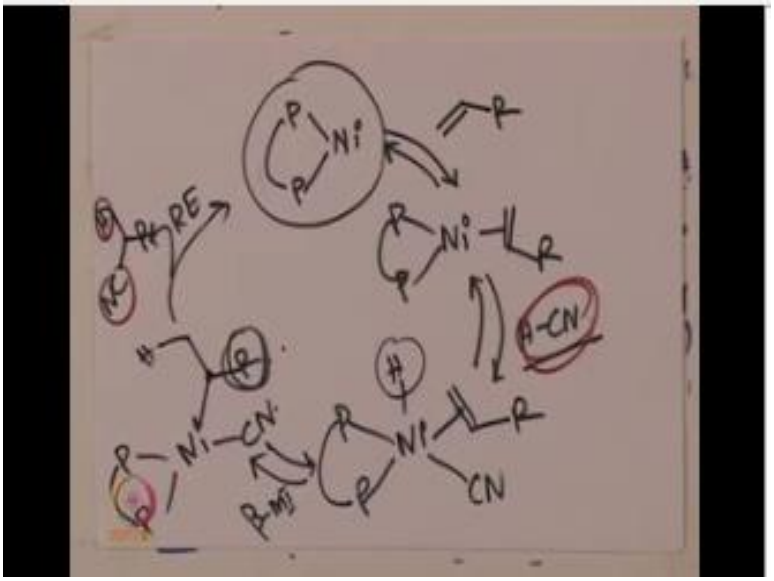


So the last topic of this course is the hydrocyanation reaction now hydrocyanation reactions are the one where we will see into the olefin molecule we will introduce a hydride and the silyl, now these of course this is not under the traditional banner of the carbonization reaction but the mechanism is going to be similar to that of the carbonization reaction that we have seen and therefore we would like to discuss this and that will be the final topic of this course.

Hydrocyanation reaction similar to the hydro formulation reaction you can have the linear version or the branch version linear product will be predominant as you have seen for the aliphatic cases if it is styrene cases then you will have the brand product once you have the brand product as the major product you may need or you may want to get the asymmetric version of this reaction and that is controlled by the choral ligand for the metal center will we will see these

are hydrocyanation and reaction particularly for one of the cases that we will discuss over here okay.

For hydrocyanation reaction the general reaction type is the one over here as you can see if you have let us say if this is the this is let us say naphthyl one or styrene l we will get the nickel as the starting material in this case and we can have that code as you know cyclooctadiene can react with Nicola with this nickel quad can react with the olefin to give you the corresponding are silos in this case asymmetric Hudson we are talking about and this meat aisle and this way when R, R can be of stydenile again Naphthenic or napthyl stydenile we can get a good ee for this reaction it is a choral bidentate ligand we can use for example for this reaction.

So the mechanism for this reaction will be as you are trying to say will be very similar to that of the reactions we have seen so far let us discuss the mechanism so nickel will coordinate with the phosphine a bidentate choral phosphine ligand let us say in this case for asymmetric version and olefin will come and interact with the nickel center to give you nickel olefin intermediate, with the phosphine coordination. so of course in order to generate this you will have to lose the, podcyclooctadiene those are not that of a good ligand compared to the bidentate phosphine ligand, therefore the ligand displacement will occur to give you the so called putative reactive intermediate.

And then therefore we will interact further with the hydro Sian hydrocyanic acid HCN and to give to give the nickel hydride and cyano equivalent, along with the olefin coordination with it, and then of course the phosphine is coordinated, so what you have seen is the first of all of course ligand Association and phosphine coordination god dissociation in Fosston, coordination olefin interaction ligand association, exogenous ligand association then exogenous ligand association, then H-CN oxidative addition, into the H-CN to give you this intermediate.

Which is Penta coordinated nickel intermediate, from here on as you can see the hydride is there allyphene is there, of course you can predict by now beta migratory insertion would be going on at this step so beta migratory insertion will give rise to your alkyl intermediate, is the secondary

alkyl because the R group is sky denial in nature, or nap file, and therefore the negative charge over there can be stabilized, that is why we do not get the linear one.

The branch 1 we are getting particularly in this case, from there on reductive elimination will predominate or will pick up to give you the desired product of the hydrous ionization reaction, okay this hydro ionization and reaction this hydride and this I know is coming from here, and that is where we are talking about that this is a Hydra scienation and reaction. Of course Hydra scienation and in industrial scale, we have we can also use these are the industrial scale reaction sometimes utilize for the for the nylon preparation actually, so for example butadiene can be reacted with hydro science, I know its CN and to give you the depot nitride design no intermediate so two olefin, two olefin attached with each other on three dying or butadiene.

Now this beta dine can be converted by this hydrosionation and reaction to give you a depot nit rile, and then that depot nit rile can be reduced to give you the diamine, diamine 12 diamino butane basically, and that 12 diamino butane can be reacted with the di carboxylic acid, to give you the nylon so nylon 66 polymer amide can be synthesized by this process.

So hydrocyanic sent as you may know is widely used in the industry specifically let's say for nylon synthesis it is quite popular you can look it up this is, this is a very simple reaction where butadiene is reacting with a Hcn to give you the dicyanobutane and from there the reduction of this will give you the, the six carbon containing amine and that Amine can be reacted with the dicarboxylic acid to give you the give you the polymer that is the polymer amide that we also known as nylon 66, that is industrial using in a huge scale and as you know these hydros iono DX area little bit tricky to deal with one must take care must be taken before handling.

Because you are going to deal with hexane, so industry has to be extremely careful to utilize so to speak also the carbonylation reaction need to be dealt with very carefully, and the proper safety precaution must be taken before doing these reactions. So what we have seen for the carbonylation and this is a Hydrocyanic reaction the reaction mechanisms are very very simple, if a the ligand dissociation ligand Association and then you know, then you oxidative addition the migratory β migratory insertion and some cases then followed by the α migratory insertion

and then reductive elimination or oxidative addition again for another hydrogen and so on as you have seen.

The fundamental steps remain exactly same or similar either you know the sequence can change but essentially you get the product formation very efficiently. Once again this is the last class I expect that you have understood the basics of organometallic chemistry and those specifically those reactions you can study from any book some of the some of these of course the ideas are some of the course organization, I of course there was influenced from my various features, but I hope I was able to give you an idea that these reactions are very, very efficient and can be utilized in an industrial scale.

Of course I thank all my teacher with whom I have the opportunity to interact and they have influenced me greatly in teaching this course and organizing this course, I hope you have taken some message and you will be able to utilize these in your in your research or for further studies with that hope I would I like to conclude this course, brief course and would like to welcome for the future courses that I will be having on the organ metallic and other related topics. Thank you very much for your kind attention and please keep studying or nonmetallic chemistry.

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