Heterocyclic Chemistry
Prof. D. R. Mal
Department of Chemistry
Indian Institute of Technology, Kharagpur

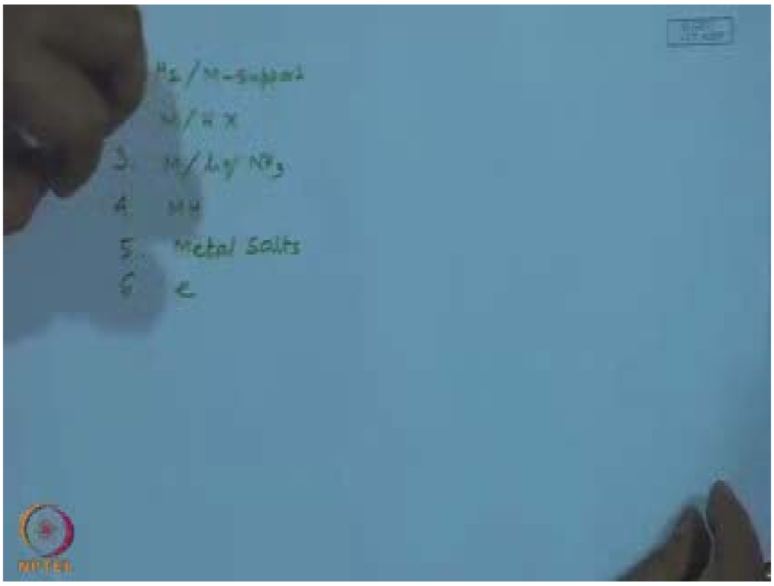
Lecture - 12
Reduction in Heterocyclic Chemistry

Ok, is understood today's topic is reduction in heterocyclic chemistry, all of us know and I do not have to any iterate that this topic is very fast. But in this class what in this class probably in the next class I will just try to summarize. And highlight the use of the reducing agents in heterocyclic chemistry whether by now all of you know there are large number of reducing agents know in literature. I mean just given idea about the number of reducing agent in only one particular area; that is a Borane chemistry; there are more than 50 different reducing agents; you staring with Borane B H 3. B H 3 simplest one, then if put it in THF that becomes 1 reagent; THF Borane complex; you put it dimethyl sulfide that becomes another complex.

Then, if you put Borane I mean morpholine that becomes another reagent, so likewise there are more than 30, 40 may be 50 different reagents; then all of you know the catecholborane, the pinacolborane then ((Refer Time: 01:42)), so like this you know. Then sec butyl Borane all these things then alpine Borane, I can tell you some of the names which are widely used then so likewise.

So, if you from move from boron to metals will fine, all the all most all the metals are reducing agent at some at somewhere at some point. So, what I have tried? I have tried to basically collect all the reducing reagents under one umbrella under in the heterocyclic chemistry, which has more often use or other extensively used. And normally by know now you know there are 4 different kinds reducing reagents in organic chemistry.

(Refer Slide Time: 02:29)



H_2 / M–Support

M / H X

3. M / Liq NH_3

4. MH

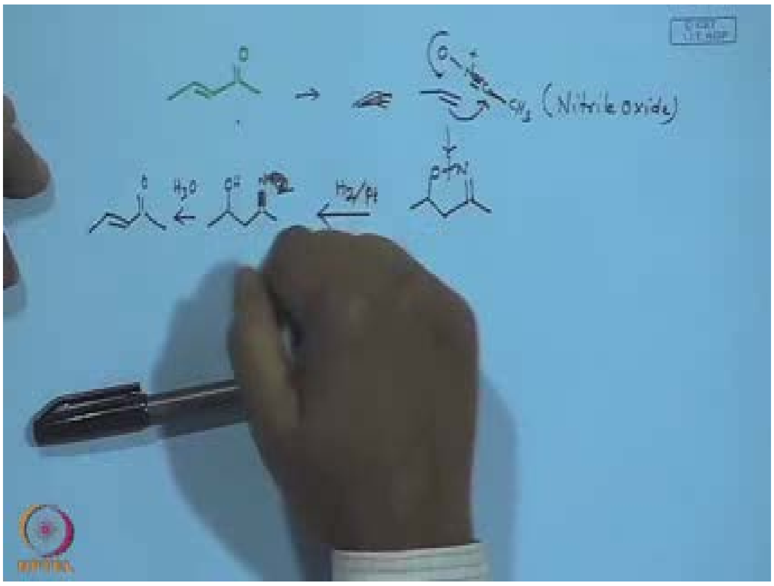
5. Metal Salts

6. e

The first and for most one I think all one of us know what is it? Hydrogen and metal; Hydrogen metal, metal supported metal and support like palladium then alumina all these things right. And then what would be the second category? Second category could be metal and acid right metal acid; third category could be metal just simple metal in liquid ammonia that is the bars reduction. And fourth one metal and hydrides metal hydrides and the fifth one metal salts that is it.

So, of I mean then up course the sixth one I mean you one can say sixth one is what is it electron; electron reduction also is quite useful. So, I mean but will ignore this because in heterocyclic chemistry the sixth one is not often used. And why do you study all these things? There are 2 reasons or there are 3 reasons I should say; 2 reasons you can do little bit of functional group manipulations that you can make use of the reduction process to make useful compounds. And third one would be use in total synthesis or in industrial processes. That means, just to briefly introduce the use of how let us say reduction in heterocyclic compounds.

(Refer Slide Time: 04:27)



And, how do you make this alpha beta unsaturated ketones apparently it looks very true real right. Because from the school life you have been studying that this is a process; there is a process called Aldol condensation one can do it. But other than aldol condensation can you think any another thing; I can give you a hint it comes from a heterocycle. So, the heterocycle could be impact, heterocycle could be let us say I have to give try this is a double bond; it is a double bond just olefin. That means, you can start from olefin and then there is a compound whether you know or not this sort of compound this is cyanide oxide. Cyanide oxide that means this is C H 3 here and then you have a triple bond nitrogen plus oxygen minus. I think I told you before it has in name call nick name what is the nick name? Quick nitrile oxide.

So, nitrile oxide cyclo addition is a very useful process actually. And this can be easily obtain from compounds often we discard in organic chemistry laboratory; oximes this if you have aldehyde and then hydroxyl I mean you get the corresponding oxine; if you oxidize with let us say sodium hypochlorite it would produce this nitrile oxides.

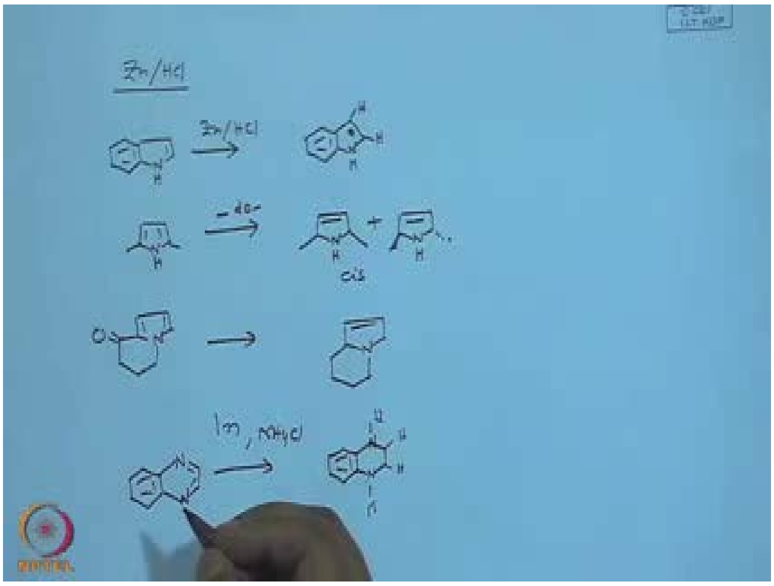
And, then if you react this and you can see from this olefin; there is a polarization in this direction and then this. So, eventually it will give you what will give you? You can see it is a process is a cycloaddition process. So, also all of you known this process is known as 3 plus 3 cycloaddition reaction; I think probably either in the next class or class of the next we will be taking about the cycloaddition reaction in heterocyclic compounds; this is pretty useful one very simple neat and clean just mix them reaction and often the religious selective and also tedious selective often.

Now, you want to make use of this compound what do you do? That means, the what you can do you can just if you think of a selective reduction minus says selective reduction means just one of the particular bonds would be reduced; neither this carbon oxygen nor this carbon double bonded oxygen only the bond that is pretty weak bond that oxygen-nitrogen bond. How do you so?

So, that is what you have to know basically this lecture is on that under particular circumstances a particular circumstance; you have to use a particular reducing agent unless and until you know then it is you have to just look around all these possible heterocyclic reducing reagents. In this case there are many I mean quite if you reagents are known in this. But if you simple the simple one I do not remember it could be either palladium, palladium nickel or platinum whichever one of them would be reducing this compound to corresponding amine.

And, then hydrogen right and sorry you should be I think this N H 2 sorry it should be double bond N H sorry double bond N H. Now, if you see so then it is hydrolyze what you will see, what you will get? You will get the one we started with this is basically there are many uses of this nitrile oxo cycloaddition; what I am trying to say this is a just an introductory slides where you see an heterocycle can be used for synthesizing so called typical Aldol type of products. And using without using without using a Orion acid to produce this aralon. So, as you have seen all ready there are reagents around 5 different kinds of the reducing agents.

(Refer Slide Time: 09:22)



Let us look at the one often use in heterocyclic chemistry that is basically be zinc H C L. And we start with a by cyclic heterocyclic system which is nothing but Indole. Now, let us see what can I do if you react with zinc and H C L? And what is a our between the two; one of this ring would be reduced. Now, we have to make a guess intelligent guess of course which one would be produced, which one would be reduced? Any idea.

Student: ((Refer Time: 10:01))

Compounding itself the heterocycle.

Student: ((Refer Time: 10:07))

Up to pyrrole ring. Pyrrole ring and what is the justification?

Student: ((Refer Time: 10:14))

Higher resolution very good. So, I think so that means the product would be this. So, benzene and higher resolution is this so that means lose of resolution has the during the processes less; if the pyrrole ring is hydrogenated. So, and this is also true if you have an isolated case. For example, isolated case like a dimethyl pyrrole. So, you do this same reaction and in this case of course the chances are that means a many but the one that is produced by the by say partially hydrogen nitrate say 2pyrrolidine sorry 3 pyrroline is produced. And then again you have probability of this is cis and then of course there are also probably that it can produce the a trans one. You get the mixture of cis and trans normally you get the trans of course in ((Refer Time: 11:25)). But in sort of reduction contractive the hydrogenation. So, I will see there are lot of cis.

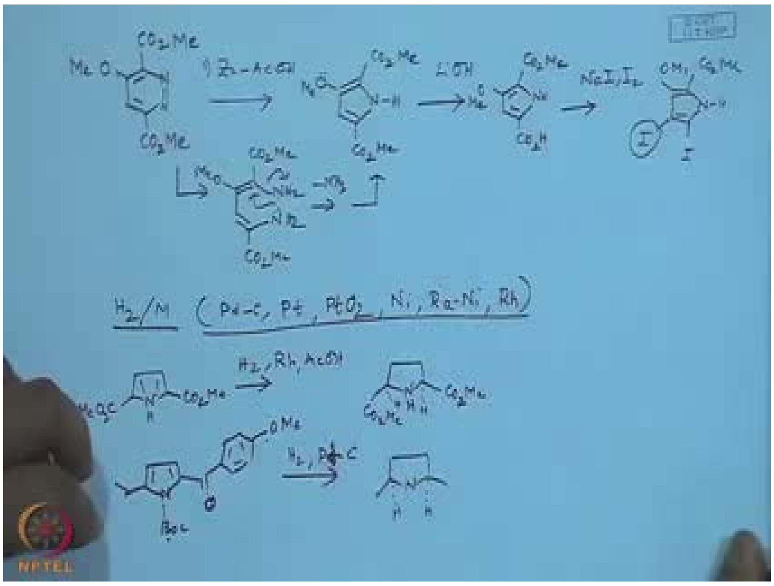
Similarly, I mean I can bond giving you example the let us say if you have a hydro aromatic systems; means part of it is aromatic other is not. And then if you do the again the same kind of reactions I think by now you should be able to predict what is a product that if you have a individual pyrrole ring. So, it is it gives Pyrrole sorry pyroline. And then you have a 6 member ring a system that is it this is a combination of the reduction as well as the so called clemmensen reaction; the carbonyl is getting reduce the corresponding C H 2 group.

And, then probably you are not familiar with some of the things like there are other metals other than zinc what are the other possible metal normally used in tin; tin is also used. But heterocyclic chemistry tin have been come cross because there is a serious problem in tin actually renewal of tin compounds; most of them, most of time they are insolvent organic solvent number 1. Number 2 if you try to remove that by acidification etcetera you get lot of flow ring lot of insoluble materials.

So, tin I have not come across; I mean but the one that is now user friendly is indium whether you know or not indium is a nice metal; indium just indium metal it is somewhat most stable than aluminum. But also you can use lot of controlled reduction lot of thing and one of the reduction that has been worked out with indium. Let us say you have quinoxiline let us say quinoxiline; then if you indium you do not have to use a very strong acid just weak acid that is a ammonium chloride; that would give you as you can see hear the heterocyclic part.

That means, this pyridazine part would reduced and what you is a basically tetrahydro compound; and there are plenty of examples. In fact, you also should know that indium is a very mild and reasonably good reducing agent for the reduction of nitro group to the corresponding amino group. And also indium is not that expensive compare to many reducing agents. And may I will give you one more example where zinc acetic acid has reduced a nitrogen-nitrogen double bond.

(Refer Slide Time: 14:21)



And, here is an example where have what is the nucleus? I thick by now all of you know the nucleus I am writing the nucleus is what is the nucleus, what is the name of this nucleus? Pyridazine 1 or 2; 1, 2 nitrogen is pyridazine. So, if you very in this case a zinc and acetic acid is reducing agent. So, it is somewhat mild but quite interestingly this would give you something like this which is a ring contracted ring that is pyrrole. And what is the mechanism? So, the is nice way of making a pyrrole and is a multifunctional pyrrole. So, what you expect here is the expectation is that achieve this nitrogen-nitrogen double bond is reduce. Now, I mean this is what is simplification but you can remember in this way this reaction has been used in many of a sense; then you have this esters here and then you can guess.

So, what could be the I mean you can either use this one or this nitrogen simply in the presence of acetic acid the ammonium comes out. And what you get is disposed that is it; and then this compound has been just quickly just review little bit of the pyrrole chemistry here. And if you treat with lithium hydroxide in the last class I talked about at one of the ester group should be hydrolyzed and selectively one thus.

And, this the pyrrole groups remains intact o methoxy remains intact; and because of this lone pair effect of this oxygen; this ester is not hydrolyzed. So, this should remain intact; and then this one would be hydrolyze to carboxylic acid that is one of the this is a just next size of selective reactivity of the 2 ester groups. But what I am trying to tell you that this sort of compound under goes peculiar reactions unlike normal aromatic compounds; if you react with sodium iodine iodide and iodine it gives a diado compound. I think by now you should be able to work out what diado compound? We see and normally if you want to do the iodozination of benzene; just simple iodination is not enough or you input iron that is not enough what you have to do?

Student: oxidizing agent.

Right oxidizing agent. But in this case pyrrole is analog us in reactive to anilines. So, under the and so with iodine it can give a product which is; so rest remain. And that is and then it gives you the o methoxy here and this. So, this is just a case where that means you can put 2 different iodines and with simultaneous clause of the carboxylic acid group. And you can mechanistically work out because mentally you can work out that iodine iodonium ionic bond; then carboxyl takes place first one this is the first one that is not did not a problem at all. Second one iodination takes place here and then dicarboxyl is deriving force that is gives you the this.

And, there are quickly next one is let us say hydrogen and metal system. And this is widely then chemistry organic chemistry; reducing agent means the hydrogen and metal. Now, metals could be all us know by now metal could be the first show I seen normally paradigm supported. Then second is second popular metal is.

Student: Platinum.

Platinum; third platinum oxide that is readily available it get in c 2 gets converted in to palladium sorry platinum metal; and then what else.

Student: nickel.

A nickel fine nickel sometime alone is enough Raney nickel there is a call Raney nickel right. And then one more ruthenium hydride I have not seen but rhodium is an often especially redust it rhodium somewhat cheaper and useful, quite useful. So, this kind of a nickel.

Now, heterocyclic chemistry also is all of these are pretty useful but the trend is little different. For example, if you want to reduce the pyrrole itself by hydrogenation is tough; you have to very high temperature, high pressure all these things. But if you have an electron withdrawing group then you can readily reduce it to the corresponding saturated compound. Example is let us you have pyrrole and then carboxylic ester here one side, other side you have a carboxylic ester.

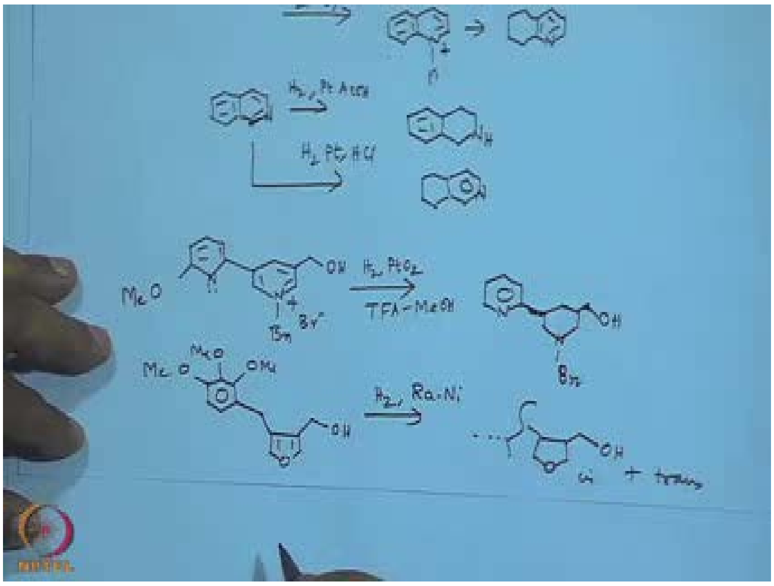
Then, if you subject it to hydrogenation the example I have here with the rhodium and then acetic acid acetic acid. And as usual this would undergo reduction to the full would saturated heterocycle that is pyrolidine derivative. And then corresponding ester; mind it the carbon nitrogen bond is not being broken the ester group the ester groups are remaining intact; there is no problem at all. And if you recall the guide line I gave you that is very useful guide line; if you have a polar bond try to use the hydride etcetera polar reagent.

If you have a non-polar that is mean carbon-carbon double bond you try to use hydrogen and all these things this system especially. And because reactions are heterogeneous; so they are often tedious selective and then it is gives you the cis one. And then next one basically example for the similar trend here you have the boc again a pyrrole; then and see here is carbonyl right. And then aromatic ring system and this. Now, the reagent here is hydrogen and platinum and carbon sorry is platinum on carbon.

So, what you have expect so many groups are there, so many groups. And especially when a group is let us say is leaving group is there ortho or para to the carbonyl they also likely to the knocked off during the hydrogenation; like in the in this case you have a methoxy here there is a like you have a carbonyl and you have also amide carbonyl. And then you have the aromatic ring here what did I say that if you pyrrole it attached withdrawing group there is possibility that the pyrrole ring would be hydrogenated.

And, the carbonyl is not getting hydrogenated so and the answer obviously I do not have I will not right the full structure; you can just write only part that the changes in changer are taking place is this one that is it. That means, the pyrrole ring is a hydrogenated and the rest of the things I remains as it is fine. So, have known; let us look at the traditional reduction.

(Refer Slide Time: 23:13)



Let us say if you want to reduce this quinoline; and you have to different thing benzene ring and this thing, that thing fine. And the condition let us say here is hydrogen and nickel and little temperature. So, what do we expect which one is susceptible to hydrogenation; between the two, benzene and the corresponding this; pyridine part. Because again this aromaticity loss of aromaticity is not more here; if you reuse the benzene ring the aromaticity is loss more. So, that means the product is here is the tetrahydro quinoline 1, 4; 1, 2, 3, 4 tetrahydro quinoline. Now, I will just many of you probably know hydrogenation can also be carried out in the presence of an acid or a base like ethylamine or other base or even tetraacetic acid, HCL.

In this example I give you a conditions where you have hydrogen, platinum and HCL. So, what do you expect? HCL is there and all of us know the proton transfer reaction is very fast reaction. So, it will immediately pick up or it will be it will not protonate the nitrogen fine; now the hydrogenation is taking place. So, that means quinoline ring becomes further electron deficient right.

So, what is the prediction? Prediction if considering the electron deficient of the pyridine part; then that should have been reduced. But you have to go back little bit as I said polarity increases; polarity bonds of the pyridine part increases. That means, immediate intermediate is the protonated one; right this protonated one. Now, this carbon double bonded nitrogen is now more polar; consequently is conjugation with a other. So, all these bonds are quite highly polar; so the reduction product that would be expected now or other in fact which found is this one.

That means, just by using acid you can divert the reactions in different transaction and this is quite. In fact, this is very true let us say very true for the isoquinoline case; isoquinoline case also the conditions are quite similar. Let us say I give you a condition where hydrogen, platinum and acetic acid fine. So, what do you expect? I will give you enough of background on the top. Now, this is a isoquinoline in case; so the pyridine part would be reduced or the benzene ring would be reduced. You can finally enology on the top it should be the benzene ring right. But the answer says it is answer says this; tell me why you know the reason acetic acid is not that a strong acid protonate to the nitrogen.

So, if you now protonate with a there are a stronger acid; let us say hydrogen and platinum and then HCL then of course the answer would be otherwise. So, I will this is a nice trick actually it to switchover. Now, let as look at a case here little different. Now, you have 2 different; we have 2 different kinds of the heterocycles is a pyridine and this is quaternised the benzyl group. And then you have OH group this is nice example the condition is here; hydrogen and platinum oxide which is known as edam’s catalyst right and then trifluoroacetic acid and methanol let us say.

So, what do you expect? Let us say this is a pyridinium ring and a pyridine ring. So, that means after protonation both the ring becomes electron deficient both the right is a matter of choice. Now, that means if you protonate this nitrogen lone pair here that means both becomes the pyridinium. But the since you have to plenty of trifluoroacetic acid it can also is the all most 100 percent pyridinium ion is found.

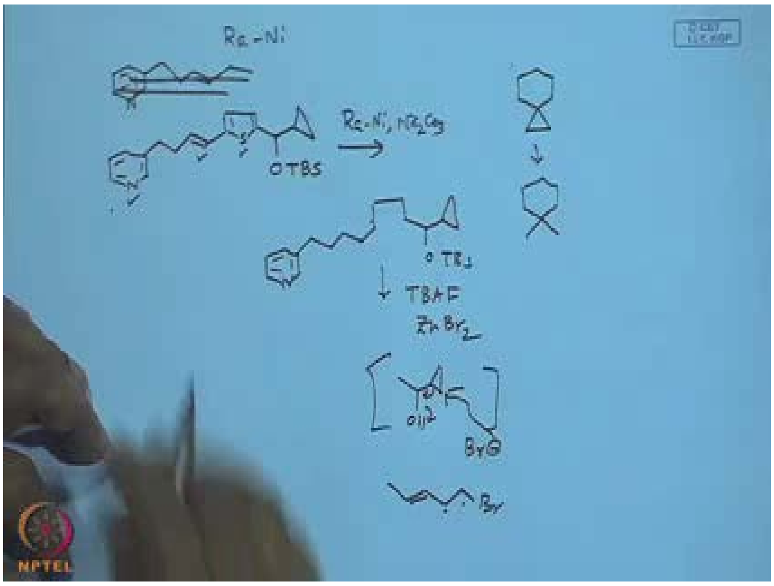
Since, it is alkyl group of here the benzyl there is a likely hood that the this character of ionic character on the right hand side ring is slightly less. And in fact in the in real life the other ring this remains as it is and this pyridinium with benzyl group with benzyl group is reduced. And as usual this substituents becomes cis just may be one more example could be let us say in this case this is competition between a benzene ring and a furan ring let us say benzene ring, furan ring.

And, you have a 5 furan and then you have all kinds of methoxy here and there methoxy, methoxy and the methoxy; as the reaction condition is hydrogen. And the catalyst is raney nickel by now you know I guess how is a raney nickel made quickly? It is made from a alloy; alloy of aluminum and nickel; aluminum react with a sodium hydroxide give hydrogen and then it absorbs. Now, I mean now I think you have a enough of a examples of this applications of hydrogen in reduction.

So, that means you have to keep it in mind whether the polarize that means polarize bond and aromaticity; these are the 2 important guide lines whether the bond is getting polarized or the bond is or the loss of the aromaticity is less in case of the hydrogenation. So, between the two you can quite obviously see right between the benzene and furan the lose would be less in case of furan.

So, obvious answer is so everything remains as it is. So, now you have a mixture of cis and transfer. So, if it is cis then other also the transits produce; so rest remain as it is rest. And what next other then we will come back may be I think to other system. Let me quickly go to another kind of actually sort of hydrogen. But the hydrogen also pretty useful; this is just say complicated example. But this example will tell you many things.

(Refer Slide Time: 31:23)



For example, I have an example it is not exactly hydrogen it is a use of raney nickel. So, raney nickel means it is a nickel and the top hydrogen adsorb on the surface of the metal. And you have now pyridine sorry pyridine then you have a side chain with double bond then you have a thiophine ring; I mean so many things. Then you have right there are so many lectures in this and TBS all of us know tertiary butyl silyl fine. And the reaction condition is raney nickel and with sodium carbonate.

So, what do you expect? Apparently nothing is mentioned means it is a sort of a room temperature kind of reactions. So, that means how many reducible groups are there? How many reducible groups that pyridine ring 1; double bond one, you have thiophine ring system one. Then you have sulfur that can you get reduced then you have cycle profane. So, many reducing but this is very specific, very selective very selective highly selective I think in last year I told you right cyclo propane it used for generating in organic synthesis many times just quickly anything you have to remember in carothors book. What you seen in carothors book? If you do the hydrogenation what you get? This is example taken from carothors book.

Student: ((Refer Time: 33:34))

Not really; gem dimethyl group which is a typical structural feature of all the typinoids. So, that means that cyclo propane and from B sc you have learning right cyclo propane behaves like a double bond most of the characters are like a double bond. So, that means you have all different kinds but the product you will get is this. That means, the pyridine is not reduced under this normal conditions by means no high temperature; the double bond is reduced.

Then, the thiophine double bond is reduced more the thiophine double bond is reduced then this remains as it is TBS and cyclopropane remains as it is. What else what you can we see that sulfur is nicely desulfurized nice this is the beauty raney nickel; so specific it can reduced desulfurized. What does it mean? That means, thiophine nucleus can be utilized to form a aliphatic chain that is it and that reduction is very special reduction.

And, then of course little chemistry not heterocyclic go; if you all books like room temperature very quick; we do in our lab also you often do. I know I mean no more than 100 degree centigrade. I mean we did it before long time 1994 you just remove yes hydrogen then sulfur from aromatic ring also yes a methylene. And then a this is little chemistry beyond heterocycle tetra butyl ammonium fluoride all of us know what is the product and distillation. Then you treat with this zinc bromite any guess, any guess what should be the product?

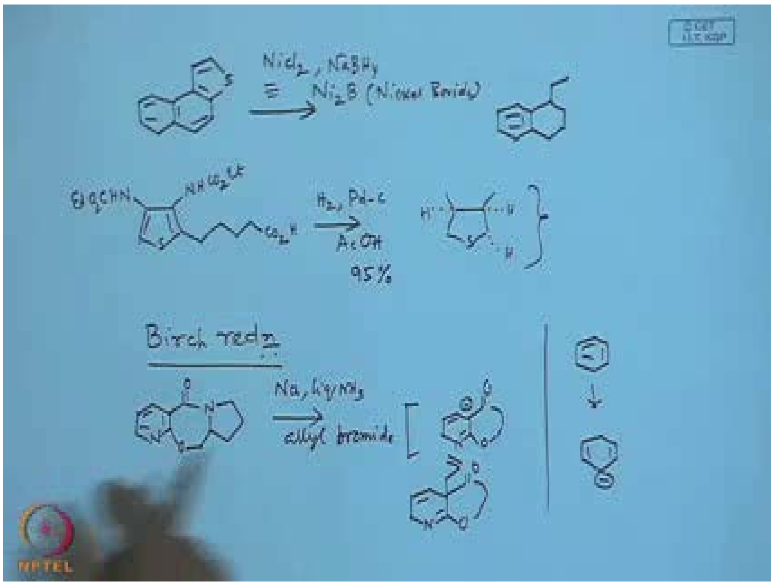
Student: ((Refer Time: 35: 49))

So, then OH is produced; basically OH is produced what next?

Student: ((Refer Time: 35:59))

Actually homoallylic bromide is produced, zinc bromite attacks the cyclopropane and this become out. So, what you will get? You will get this is allylic, this is homoallylic these are I mean nice chemistry; so but all these chemistry could be done. Because of the selective reductions of this raney nickel. I can give you one more example probably; one more example raney nickel is such a nice compound though is a nice reducing agent.

(Refer Slide Time: 36:46)



Let us look at one more example where you have a thiophene nucleus is a naphthalene moiety and a thiophene nucleus and this. Here, what you use? You use nickel chloride and sodium borohydride; what is it? It is equivalent to let us see all these things are taken from Monessen bird Solomon is not very high level chemistry we have been talking about very low level chemistry.

What is it?

Student: ((Refer Time: 37: 27))

Nickel boride the formula is N i 2 B; I do not know why N i B 2 but this is the formula given by all the books; this is known as nickel boride it is somewhat equivalent to raney nickel. And so obviously the answer of this reaction product of this reaction is this; so ethyl benzene. So, nice reaction I have more examples if the time permits we will talk about. And next let be may be will give you one more example this also tells you many,

many things; again a thiophine. And then you have any carbonate side chain again a carbonate side chain; then you have a side chain up here with a carboxylic acid; do not worry about the number of the carbons of the chain. Now, the reaction condition is hydrogen and palladium carbon the solvent is acetic acid; and the whatever the reaction product is in excellent yield 95 percent.

So, what do you expect? This is a basically this is our job we have to gather some knowledge, you have to extrapolate some knowledge; you have to predict something. So, we have so many reducible groups; you have a carbonyl up here, you have carbonyl up here, you have a carbon sulfur bond, you have a carbon double bond nitrogen, you have a carboxylic acid. So, all of us know hydrogen is not suited for the functional group transformations like carboxylic acid, amides, etcetera. And possibly double bond and this thing and many of you already know that these palladium often gets poisoned by sulfur, quinoline etcetera.

So, you have a sulfur here; that means sulfur is not knocked by the palladium catalyst. But it can assists the hydrogenation; that is the difference raney nickel can knock of the sulfur. But this one that means the product that would be formed here is this. And so all the hydrogen are sis now added hydrogen are sis and rest remaining as it is. So, when I write bracket means rest of the things are as it is. So, sulfur is not out because by use of palladium.

What next? Next is very important what next birch reduction. Birch reductions you have learned is a very, very useful reactions. In fact for a long time this reaction was not used in heterocycle chemistry very few, very few scientist reduce of this one of the person who used is I think I will tell you the name Donohoe ice from Cambridge; he still using this reaction heterocycle chemistry it was not that equivalent; and but all of us now. Let us begin with the simple one of the latest examples of birch reductions of the heterocycle molecule say pyridine nucleus of the carbonyl up here then 4, 5, 6, 7; 7 member ring then you have a 5 member ring.

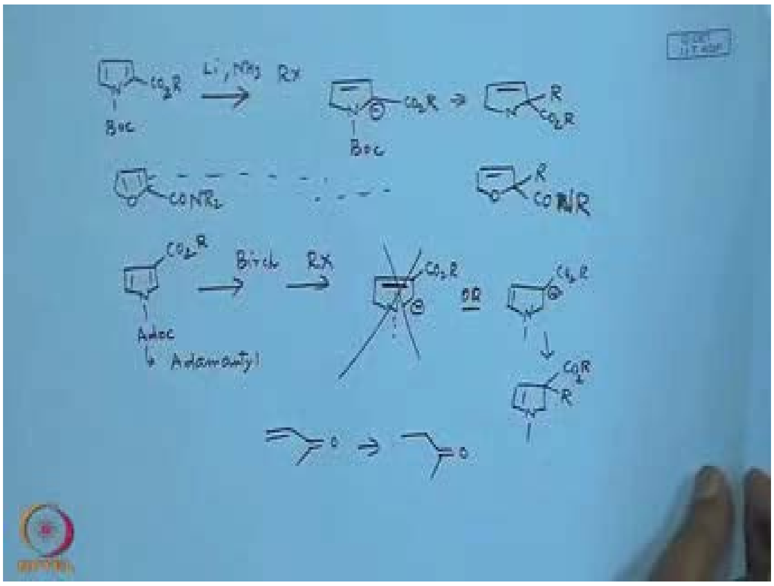
So, you can see that you have a pyridine nucleus. And on this middle you have ordinary nucleus by now we should be able to now ring should named as quick what should be the name oxazepinon, oxazepinon 7 member ring oxazepinon; the metals in by birch reduction normally metal birch reduction metal sodium or lithium very occasionally people have used calcium; I mean ((Refer time: 42:12)) university used that.

Let us see so lithium sorry sodium and liquid ammonia liquid ammonia is a solvent of course. And then what you use allyl bromide? I think all of us know the reason what is the basic background? The basic background is that if you have a benzene birch reduction is a process is a dearomatization process; that means double bond. That means, what you will get? You will get this one cyclohexane 1, 4 diene right 1, 2, 3, 4 cyclohexane 1, 4 diene; this is d conjugate process.

In fact, very recently one paper has they have done sort of a Diels-alder kind of reactions the diene and a triple bond and in the presence of an organo metallic. And they have produce this 1, 4 diene system any case. But if you know the mechanism this is simulate to transfer it goes through radical anion then eventually is goes to anion. And then the reactions also is coincide with tertiary butanol; then the proton is abstracted. So, the product is formed.

So, that this is this you have to mind. And what is the driving force for the reactions? The carbon ion stability. So, if you know this basic mechanism; then you should be able to predict, what is intermediate? The intermediate should be and anion should be here that is a of the carbonyl. And that is so then the product of course you can guess whether the product would be allied would be incorporated in the anionic center. And the rest as it is this was still published by Jonas Pande of n c l this year sorry last year.

(Refer Slide Time: 44:23)



So, likewise that Cambridge scientist have made use of the reduction again of this pyrrole unit. So, you can guess what should be the ok. So, here what is the equation, what is the requirement? The requirement is that you have to have an electron withdrawing groups because that makes it little electron sink. And then the normal catalyst or reagent that is lithium and liquid ammonia; and then if you have RX; now we can guess. So, you know that the mechanism actually leads to a carbon ion. Now, carbon ion is stable at adjacent to the carboxylic ester group and so that is so that means and the boc is say this amide basically.

So, that means what we will see? We will see this anion would be at the ester alpha to the ester; this is ester here. And the product of course as usual the product would be this R here then ester here. So, what you get is a pyrroline means dihydro Pyrrole the same thing I mean this is exactly I mean is applicable also this is applicable also to the furan compounds also you will get this furan up here, and this R, and in these case the example that I have seen that with amide.

So, that means what it means that pyridine, pyrrole, furan all the 3 nuclei if their electron deficient can be reduced by birch reduction to the partially hydrogenated products. And I have one more example probably I think I will comeback little later; this is typical as the same example. And then one more I think I will give you one more example may be from birch reduction.

This is let us say now there is a little change. For example, suppose you have a substrate where ester is at 3 position and then you have a protecting group call Adoc. Now, it would be the birch reduction and then and RX. And what right?

Student: Ad.

Ad means Ad stands for actually Adamantyl and adamantly oxy carbonyl. So, now the question is the product whether the birch reduction intermediate would be like this or what? Well, truly speaking I mean this is not this not dearomatized I mean this can be equivalent to somewhat dearomatized; not only that it is a alpha to the ester group. So, in these case; this is a special case and this case this was this formed and then of course when you have RX. So, this nitrogen is not alkylated because you have this amide group here, adope means amide group. So, you have this ester group here and the R is attaches to the alpha to the ((Refer Time: 48:50)).

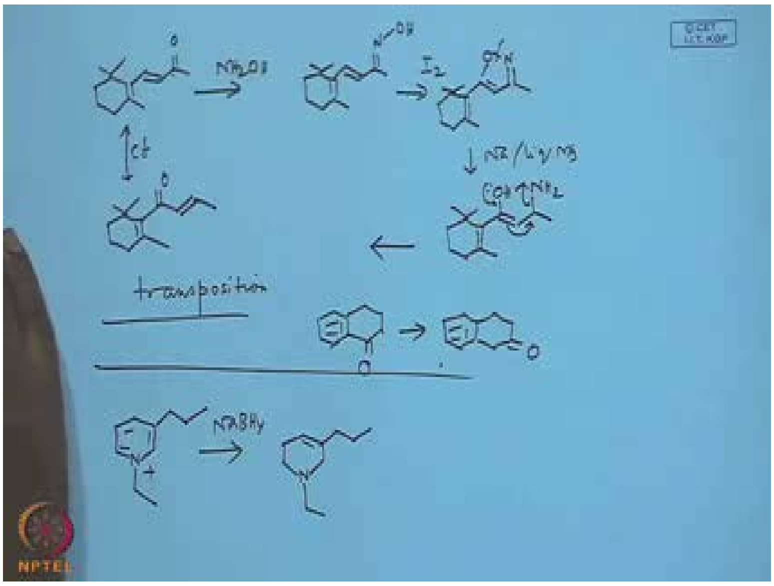
Student: ((Refer Time: 48:51))

Reason is only that ester is getting stabilize with the sorry carbon ion is stabilize by ester.

Student: ((Refer Time: 48:58))

Dearomatize see in these case is not dearomatize; it can undergo further reaction. That means, had the reaction taking place the conjugate to the ester group. For example, many of you know if you want to reduce this to the saturated one; the quick the very convincing way is to use the lithium and liquid ammonia. Because this birch reduction is not only used for the dearomatize of the aromatic systems; you can also that is way the birch reduction is defined as deconjugation; this conjugation is a broken had this been form this had given fully aromatic system sorry fully dearomatize or fully saturated system; that is one of the reason I mean since I know the answer. So, I can argue that probably because carbonyl is stabilize for the ester. So, this is like plus it is tested by the alkylation study, alkyl group enters the alpha position. And so I mean then let as there is an another example also I can give you.

(Refer Slide Time: 50:29)



Let us see this a kind of birch reduction elsewhere also has been used; this is a case from the torpedo chemistry, you have an alpha beta unsaturated system and like this. And if you have this reaction with hydroxyl amine. So, all of us know what would form? It would form the corresponding oxime right oxime should have ((Refer Time: 50:54)). But any case I will write trance I use that. Then if you treat this with iodine actually it forms it forms fine isoxazoline; means and we have a double bond we have cyclohexene ring system and this is. Now, we have generating basically new heterocycle isoxazole. And if you want to reduce this selectively this one; what reducing agent would be use, what reducing agent?

Student: ((Refer Time: 51:47))

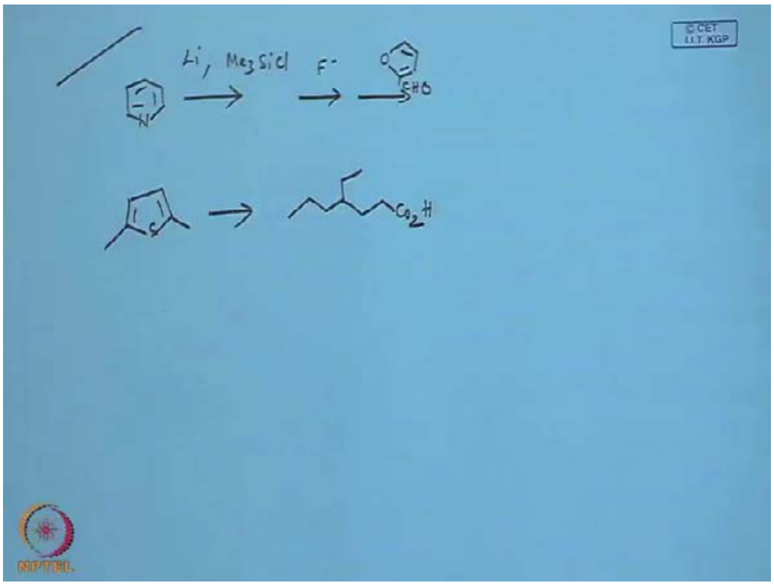
You have a carbon carbon double bond. So, this situation is different normally metal acids zinc acidic acid etcetera, etcetera pretty useful, but and but in this case sodium and liquid ammonia has been used. So, what you will find? That means, this one is selectively reduced and selectively reduced. And so this is OH then what? Then tautomerize but mind it stabilization is so powerful is a driving force, it can knock of the amine group.

So, result is everything remains as it is and you have a carbonyl up here double bond and this. If you compare this one right what is it? What you see what is the transformation isomer? So, is an isomerization the best way to this is a synthetic this is called trans position means you just exchange the positions that is called transpositions; like one of the papers in literature you will find this is a case I think this is often like it. Because this is from my area and I think I told you before this is called transposition; the methylene has been exchange to it this C O group this is called 1, 2 transposition; this is called 1, 3 transposition; 1, 2, 3 quite a few review articles. And let us give you one more may be example. Let us say this is last case metal hydrate we have not talked about the metal hydrates right.

So, that means what you need is a polar bond if you let us say pyridine and alkyl group up here. And then you have cyclic chain; then you react you want to let us say you want get to the compound something like this sorry, so partially partial redaction here you have the carbocation here. So, what reagent would you choose? We have 5 different categories hydrogen, paradigm just simple then hydrogen metal. And low metal, low valence metal salts then the hydrides and obvious choice is here is polarize bonds so it be a metal hydrates.

And, this is ring what simple sodium borohydride; sodium borohydride would be reduce this to tetrahydropyridine. And let me quickly I will give you just last example you have to tell me the answer next class.

(Refer Slide Time: 54:58)



This is from a nom next class means after next sem, fine. This is little bit of the from the silicon chemistry, let us see. I think you have learn silicon chemistry from kalser’s book is a very good book; the plenty of silicon chemistry. If you treat this with lithium and then excess trimethylsilyl chloride; then you give may be some fluoride is possibly some fluoride, possibly I do not know. Assume that there is a fluoride and furfural is this electrophile, furfural is the electrophile fine. This is one example, this is at one homework; it is not included in the example.

So, this suggest a suitable product that will comply with this reaction set. May be I will give you one more; I think this one we can do it now. Let us say how can we convert this to this? I have many more examples there; I have many more example because this is a vast course. Basically, what I said there are 5 different kinds of the reagents; one is the hydrogen metal, one is this hydrogen sorry metal acids; then metal liquid ammonia, metal hydrates and metal salts. Metal salts means normally I said nickel, boride and then sodium boride or sometimes lithium boride, aluminum hydrite; occasionally there is a new reagent also many of you know Samarium Iodide. Also, occasionally used; any idea, let us say how do you do? This is the last one for example. And what is the example for? Example for the illustration of?

Student: Raney nickel.

So, Raney nickel what does it do; it knocks of the sulphur as well as removes the double bond. That means, you get a saturated system. Now, if you do electrophilic substitution reactions on the thiofin unit; so you can get the introduction of the groups here. See, these two positions are blocked. So, if you do the electrophilic substitution reaction 3 position would be occupied and then do all kinds of requisite transformation.

And, then eventually you do use Raney nickel; because Raney nickel is very specific for sulphur and double bond. And it will not touch the carboxylic acid. So, this is a case of when I say lithium and TMS Fluoride, what is the case? This lithium and Trimethylsilyl fluoride, what is the reaction? See, in the Birch Reduction case, but I will give you the hint. I think that would be actually all of us know Birch Reduction goes through anion, but in these case 2 silicones are incorporated, this is the intermediate; disilylated dihydropyridine. So, now suggest you know what is the next product? It is a combination of two different reactions, so but.