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

Lecture - 18
Magnesiation & Zincation in heterocyclic chemistry

Good morning, in the last several classes we talked about organ lithium compounds. So, if you think about the predictable now, we have to move to little heavier atoms and next atom is magnesium. So, in today’s class we exclusively talked about Magnesium and Zinc, we will give you some of idea about I mean the position of magnesium and zinc in heterocyclic chemistry, but you can think of a greater use of both magnesium and zinc in your future. Simply because, there are many more new methods are coming up. And the methods for preparation of oregano magnesium and oregano zinc compounds.

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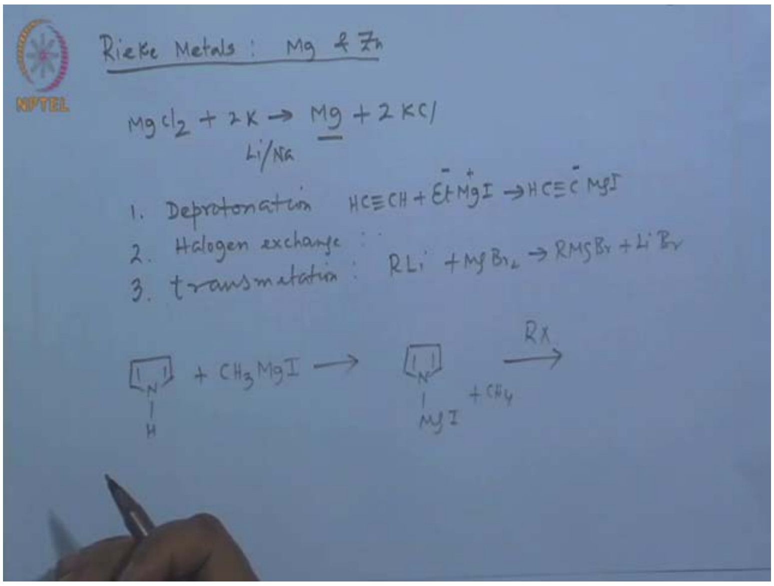

Rieke Metals : Mg & Zn

$MgCl_2 + 2K \rightarrow \underline{Mg} + 2KCl$
Li/Na

1. Deprotonation $HC\equiv CH + \overset{-}{Et}\overset{+}{Mg}I \rightarrow HC\equiv \overset{-}{C}MgI$
2. Halogen exchange :
3. transmetation : $RLi + MgBr_2 \rightarrow RMgBr + LiBr$

And to begin with I will just introduce, you to a very active kind of metal and which is known as Ricke zinc or rike zinc, ricke metals if you go to the Wikipedia they will say ricke metals, but for us magnesium and zinc should be all right, magnesium ricke is basically an organic chemist and he is, in the university of nevrask linclon USA. So, his till is a professor, but he has open to able also an industry, how to make reactive metals. For example, magnesium is not known to react with the double bond, carbon, carbon double bond, but if you have very highly reactive magnesium it can react, provided the conjugated one.

For example, it can react with butadiene, to form cyclic magnesium compounds, magnesium intermediates. What is the specialty, specialty is nothing very simple that you take magnesium salt and then reduce it with a metal, unlike electrochemical preparation. And in this case, if you say potassium, so all of us can guess, this chloride and in the place of potassium also one can use lithium or sodium. So, provided is the tricks lay in the preparation of the use or conditions whatever, but the net result is that look at this active magnesium.

So, this active magnesium is used, for the preparation of magnesium compounds, so all of us know, the typical organ metallic preparations, require I mean fundamentally three different methods right, one is very first one is how to make an organ metallic compound, the first thing that which comes to our mind is deprotonation; that means, it remove a proton. So, by which one can produce a magnesium an organo magnesium for example, all of us know right, if you have acetylene, if you react with magnesium iodet. So, all of us know, what is the product again a new oregano magnesium compound.

So, new oregano magnesium compound, so this is, then next important thing is could be halogen exchange, so this is exchange with halogen, we will talk about examples today. So, begin with, but in the combination has to be right combinations, means the oregano magnesium that would be produce should be weaker Nicole fire, weaker base because, these are the basic condition, all these organ metallic actually are refer to as base or basis.

So; that means, the reaction would proceed in the power direction, provided like in these example, in the previous example, for example, on your left hand side you had a if oil magnesium iodide, and right hand side this. Now, if you compared the if I will minus and acetylene minus, which one is more stable all of us know, stability goes to acetylene or less basic, less Nicole fire, so this is the pattern, so halogen exchange also fallow the similar pattern.

And the third option that is, applies in this particular example, what is the third option all of us know by now. What is third option preparing an organ metallic compounds, very good lithium case it was not there, that is the lowest latest metal. But, in this case, you can use it transmutation; that means, for transmutation in the case of magnesium, only option you have is the lithium. So, if you have a oregano lithium compound, oregano a lithium compound and then you have say, magnesium bromide. So, what you are like you to get, this and lithium bromide.

So, like these you can go on, if you want to make a some zinc compound I mean you can take oregano lithium or oregano magnesium, then add transmutation are normally, go in he favor of the heavier atoms, heavier and less electro negative, electro positive atoms that is the trend. And now, coming to these heterocyclic chemistry, I think very first thing that we should talk about. In the case of say for example, payroll.

Now, let us look at the feasibility of this reaction, methyl magnesium iodide which is commonly made. So, what kind of reaction do we expect out here. Normally, methyl magnesium iodide is nucleophilic in nature, but very first thing we should consider is the deprotonation reaction or the halogenic exchange reaction though they are the first reaction. Now, we have an active proton here, weather we should think about it; that means, is it a possibility, instead of the hydrogen, if you have magnesium iodide the other thing is methane.

So, is it a possibility, how do I know the feasible basically, you have to think about the acidity. An each acidity between an each acidity and methane acidity, which one is all of us know, which one is more acidic payroll hydrogen is more acidic. So, the corresponding, magnesium compound would be resulting from this reaction is that particular lane. Then this problem now, if you want do a reaction for example, let us say R x, so R x.

So, there are actually several options, how many options there are clearly three different options 2, 3, 1, 1, 2, 3 all this nitrogen can be alkulated, c 2 can be alkulated, c 3 can be alkulated. And in fact, and this is not very good reaction for the payroll chemistry, if you think about this oregano magnesium and all these three different reactions are reaction products are known in the literature. Now, go to the; that means, it is not very encouraging, while there are people have tried to optimize the reaction conditions. By, changing the solvent, this thing and that thing by eventually, but reaction is not a very clear cut reaction for.

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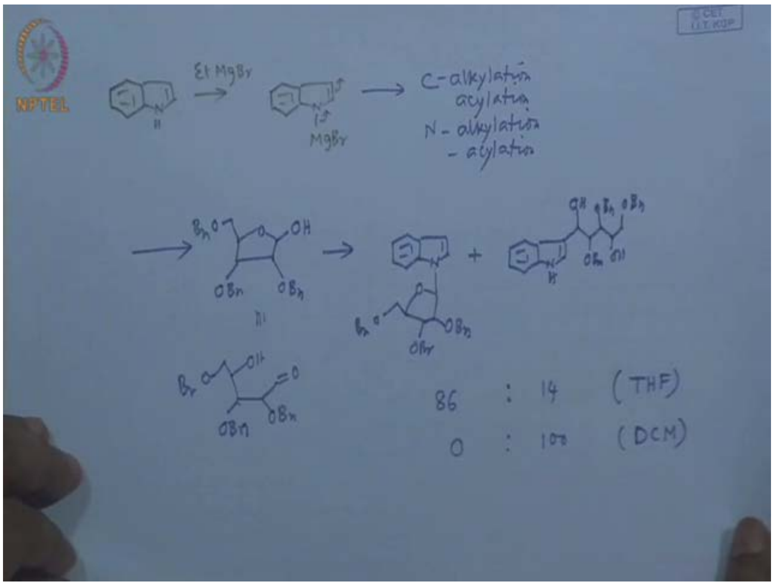

Then; obviously, what is our next option, next option is in dole. So, after payroll next option could be in dole and as usual. So, if you take, let us say ethyl in this case, ethyl often is used because, ethyl is prefer to methyl, in generating oregano magnesium compound simply because, little bit heavy little have boiling that is it. So, easier to handle methyl bromide. So, now, what we will see, that one of the options now, reduced.

So, you have now payroll magnesium bromide sorry in dole magnesium bromide. So, an all of us know, due to the redolence this in dole reactions takes place the c 3 position. And there is also a possibility that the reactions and also can takes place; that means, there are two possibilities c alkylation, we can say right c alkylation’s acylations, all these possibilities are there. And similarly, N alkylation and acylatyions all these reactions are possible.

I will just giving you one example, if you react these magnesium compound with a ribose sugar, I will not indicate the cyo chemistry make it simpler, so if right this benzyl protected ribose sugar and these. So, you are likely to get two different products, likely to get I mean two different products or we can say four different products, all kinds of products. But, in this particular example, that two different products have been found, one of them is an alkulated product, an alkulated product and the product again a ribose compound and then benzyl, benzyl and c s 2 benzyl.

The other possible product is now c s, c alkulated or c products. So, activation and Benzyl open tune compound, open tune compound. So, you should be OH then benzyl, benzyl and this one is OH. Now, I think you can explain, very simply because, this is nothing, but if you rewrite this is nothing, but it is an OH of here and this is nothing this is basically an aldehydrate all of us know that sugar is an aldehydrate and an equilibrium they exist that aldehydrate. So, basically that means, starting material it self has dual reactivity.

And after the reaction you for, we can get cyclic and anti cyclic compound, all of us know and then addition there is a possibility that a n alkylation takes place or c alkylation or c acyltion takes place. All these possible, in this particular example that these two compounds have been identified, but striking thing is that both are produced, but unequal amounts and this first one is producing 86 percent, 86 to 14 ratio. And the solvent used was THF by choosing this example, just I like to say this oregano metallic reactions, are very sensitive to reaction conditions, temperature as well as solvent.

Now, if same reaction, if carried out in DCM dycloro methane and you get c here, you get exclusively c products. So, that’s basically that is the point; that means, if you are handling with them oregano magnesium compound, there is a reaction possible with ambient nullifier. So, the ratio of the products can be changed probably by changing reaction conditions.

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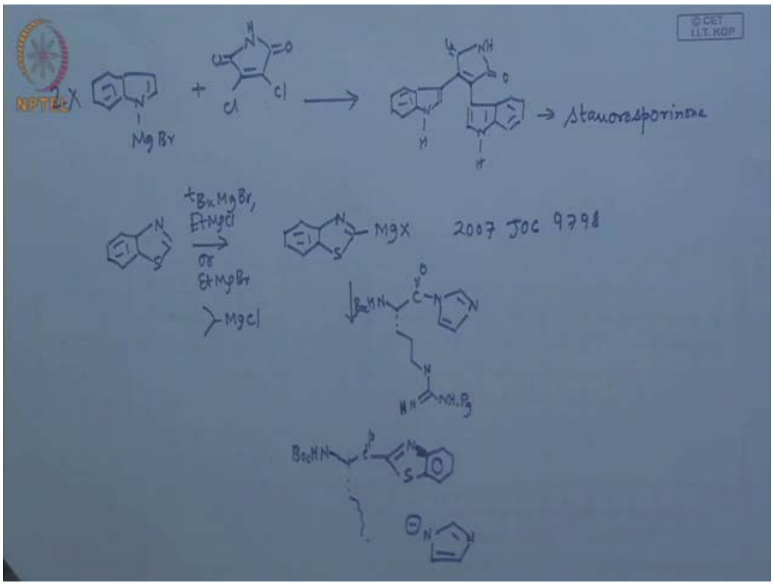

Now, look at similar reaction, but little different, again you take in dole magnesium bromide and in this case reactant is emite, sucseen emit and then substituted with two chlorine items. So, nothing no asking, just basically they are mixed together. So, what do you expect, the I mean now you have to look for, this is highly acidic, this nitrogen is highly acidic because, emite. So, it can destroy as part of it, then what else possible, then emite carbon is not very reactive towards this is not we all of us know.

So, that is the difference between oregano lithium and oregano magnesium. So, one of the reactions is basically indicative of, the unit of reactivity, we will come to that later. While we talk about, oregano lithium and oregano other metallic compounds, what is the marked difference between the two classes oregano lithium; that means, oregano lithium has a specialty that, they are very reactive. At the same time, you can control the reactivity that’s the advantage with oregano lithium compound.

And like, you can do the transmitation you can reduce the reactivity, you can reduce the temperature, you can moderate the reactivity all these possibility. So, any case, in these case already by having the magnesium, itself is quite less reactive. So, and; that means, nucro folic addition is not taking place and only addition and elimination reaction takes place, at the site of the chlorine. Eventual result is a molecule, you can this is, so of course, it will require twice of this magnesium re agent and this is hydrogen, this is hydrogen.

Many of you will be wondering, why such reaction was taken up and there are all possible reaction with oregano magnesium, actually if you oxidize you get this, you get 1, 2, 3, 4, 5, 6 you get basically a carbogen kind of molecule and the molecule eventually is elaborated to, a molecule known as staurosporine known is staurosporine known advance intermediate for every national product, but you don’t worry about this, little more complicated term on these. And, so now, let us; that means, the let us what next again restrict our examples to oregano magnesium and 5 membered.

For example, if you are to make benzothyzal, oregano magnesium compound, something like this x. So, what re agent would you choose, what re agent would you choose that’s important. And you know what procedure would you adopt, I have always said that this for generation oregano magnesium, deprotonation trans halogen exchange and transmitations. So, we have already seen that, we have already seen that this 5 membered hydro cycles is active hydrogen can be deprotinated with lithium agents.

So, you can do the transmitation, but in this particular example you don't have to, why should you in corporate lithium which is more quite expensive than magnesium. So, if you have directly, can comfort these as perfectly all right, so how do I directly do this, what are the agent available. So, for you have seen, methyl magnesium bromite, but typically actually, this typically in this example that's binkle magnesium bromite, could be use ethyl magnesium chloride, could be use or ethyl magnesium bromite could be use, and there are many instances, where you can use also this is very popular agent isopropyl magnesium chloride.

Which is readily available, isopropyl magnesium is cheaper than many other hello genetic agent. And, so one of these things would do, then once you have this, you can you know, you can go to this rest of the typical reactions of the oregano magnesium compounds, this particular compound was made in a scale of 10 k g, do you understand the meaning. Listen be it, is actually safer it is used as reactive agent in a pharmaceutical industry, if you are interested I can give you the reference, this was probably in 2007. JOC and 9798 page number by giving what I mean to say many did not can be done in kg's.

I have seen a reaction called bards reaction, I did not know whether you know or not bards reaction is done in liquid ammonia by adding lithium or sodium. Lithium is less violent, but as you go to sodium, it becomes more violent, but they just dumping kg' s of kg's of sodium, in without taking just in madras. The chemical company called orchid chemicals, how many do you know orchid chemicals, no madras, Chennai. If you go walk in the city madras depth tower is, so be you can see from distance any case.

So, this was reacted with the, compound I will just in short will right, then you have to predict what could be the product, apparently looks like a amino acid deteriorative and is 5 member nucleus, I think by all of us know, what it is then NH Boc. And amnesia means, this is an world define steroid chemistry, then here you have one more m o t NH and I think, I write P g to every where P g is protecting group and NH. So, this is the other reactant, I think by have you recognize what is the hetero other heterocyclic munity eimidazode fine good.

So, actually after the semester you will forget. So, that’s why I am asking this. And this part is known as guvaneady; that means, there is a centre of amino acid, there is a centre of this thing and this is goovanedy and you have a now, hetero cyclic reactant agent. So, we have to predict the reactant product, so what is the product do you expect. So, where do we start from, oregano metallic’s, they go for abstraction of porotons, the addition and displacement all these things.

There is a possibility normally I mean the conditions are mention, want to able to predict this whether this NH is sufficiently acidic or not, one nitrogen is not very acidic all of us know, goovanady is a base. So, it is likely to be not to be a were highly active. So, what are the other active hydrogen NH Boc, hydrogen could be acidic, sufficient acidic hydrogen. Other possibility if the reactions are prolong, like in the previous example if you recall the sugar o h e was free.

So, if you have excess of ((Refer Time: 22:01)) consume the o h e hydrogen and then rings openca becomes aldehyed then ascenx takes place. So, like wise the reaction possibility, and what is the possible reaction, the possible reactions one of the possible reaction. Now, is one of the possible reaction would be, this benzothyzole this nitrogen and this amino acid part NH and Boc and rest of the things here. So, this is a possibility.

Now, first of all you have to identify this is a possibility or not, how do you know, how do I know so; that means, this is a reaction possible, then that the group that suit come out each this one emida zone. Now, this is the possibility how do I know that same old thing, that it should produce a weaker base and weaker base or not that was have to, now you have enough of heterocyclic chemistry knowledge.

So, in the previous case it was also a 5 membered heterocyclic two atoms, right and in this case also 5 membered heterocyclic two atoms. But, mind it this the acid corresponding to the benzothyzole is CH SP to CHS and this case you have NH hydrogen and that two again payrollic hydrogen. So, all of us know payrollic hydrogen, is more acidic than any other I mean corresponding and because, payroll forms are to potassium metals etc, etc, etc, such a nice in potassium hydroxide is sufficient to extract the protons from payroll NH. So, these are the thing you have to remember.

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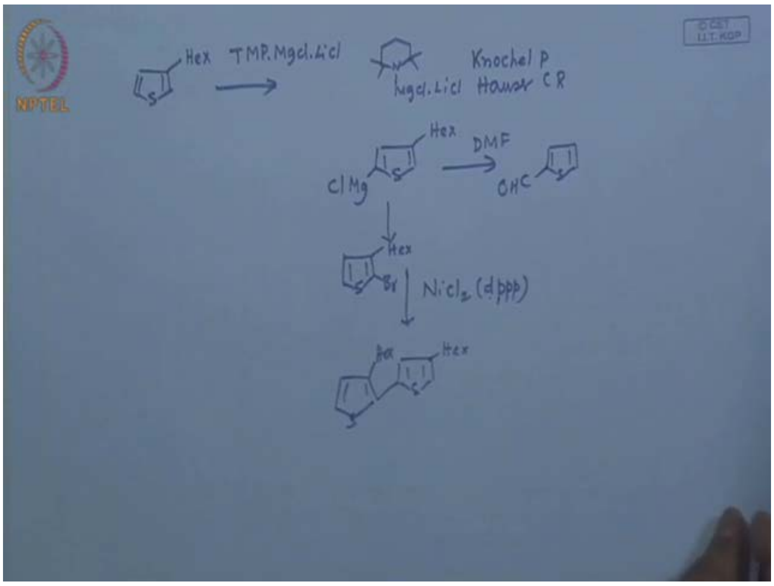

So; that means, the reaction is quite feasible 1. Now, next will take up one more very important nucleus again. This nucleus produced in kg's and kg's and tons and tons and this is a basically raw a starting metal for oligothiophene have you heard of oligothiophene have you heard, what are the famous for louder, conducter ((Refer Time: 24:37)) become conductor fine, yes very useful, very useful oligothiophene and poligothiophene are very useful for conducting material, it can be made use for preparing you know an organic transistors. Then thin films conducting fill films all these things.

They produce these poligothiophene and oligothiophene are produced in tons again in tons, that what one of my student say to work on this. And these case, what is c there is a exile m t, exile m t is basically is required for make it a processable, means solubility problem is removed. Now, if what to make a grinder, in this case gridner has been the gridner that have to be used TMP and magnesium chloride and lithium chloride.

TMP magnesium chloride, lithium chloride I think do you know, all what it is esititemethyl pyperdide, esititemethylprepidide and this is magnesium chloride and lithium chloride. This is very popular base, this is very hindered base, reactive base sufficiently reactive as you will see, in a minute is a very reactive base and this is, recently be known as paul knochel is a germen scientist, paul knochel. So, actually it is known as knochel and hauser, this hauser is CR hauser ((Refer Time: 26:28)) something like that it is very old person.

So, it is now known as, knochel hauser of this. In the previous class, we learned new base call fort base and now this. So, these are all the composition are different, but these found to be very useful and if use this base, and this person knochel I think he is I think he junior to me by, may be by 2, 3 years and he was in USA for sometimes then he moved to Germany and through out his life he is working on this zinc and magnesium, zinc and magnesium.

So, you see there may be, so much do know, in this field and he has popularized oregano magnesium’s in different fields and also recently he has synthesized electrician NSL products. So, once you do this, what do you find there are striking waves here of these re agents, one of them is deprotonation, we can directly deprotonate and produce this magnesium reagent, that is grinder. At we have to note here, it give us unless electively one hydrogen and all of us know, the hydrogen adjacent to be hetero atoms more acidic in nature and, so one of these two hydrogen.

But, also one can just quickly this because, of pyperdide steric bulk, it is not approaching the position 2 position. So, it is approaching the 5 position, so it can be steric bulk also can be made use of selective deprotonation or magnsians that’s it. So, once you have these, then you can do all kinds of things for example, you have this all of us know, but you see, you have to know note few minutes ago I said, that this oregano magnesium’s are not very reactive towards emite.

But, again now I am telling that while, so in this case DNF is nothing, but is a pharmalating agent. So, in these case it is reactive, that some of the tricky reactivity we have to take note of that’s it because, it is a 5 membered hetero cycle. So, it is a five excessive. So, it is likely to be more need to than simple aromatics, and now I mean what is how to make this oligo. So, if you take now, one more terrapin then it just couple them, that’s do we call coupling right.

So, in next class actually we will talking just summarize because, some of you know all these coupling, but just summarize what the couplings have and, so cross couplings. So, we have two different heterocyclic m o t is just couple them, but in this case it is magnesium. So, you have to also remember some of the things, that which particular conditions are require for the magnesium coupling, one of the coupling last class I talked about right, kumada coupling, kumada coupling requires iron, but also this is a basically any kind of coupling with magnesium the agent or oregano magnesium agent are known as kumada coupling.

And in this case, the re agent that is used is nickel chloride and d p p p, I think by know all of us know right, any research caller you know d p p p, may be diphenyl; that means, diphenyl first if you progrent. So, what is the result, the result is x and appears, then you get advanced monomania, then that can be polymer that can be polymer. So, what else one or two more may be I think, I will just skips on the examples they are typically that extension of what we have talked about.

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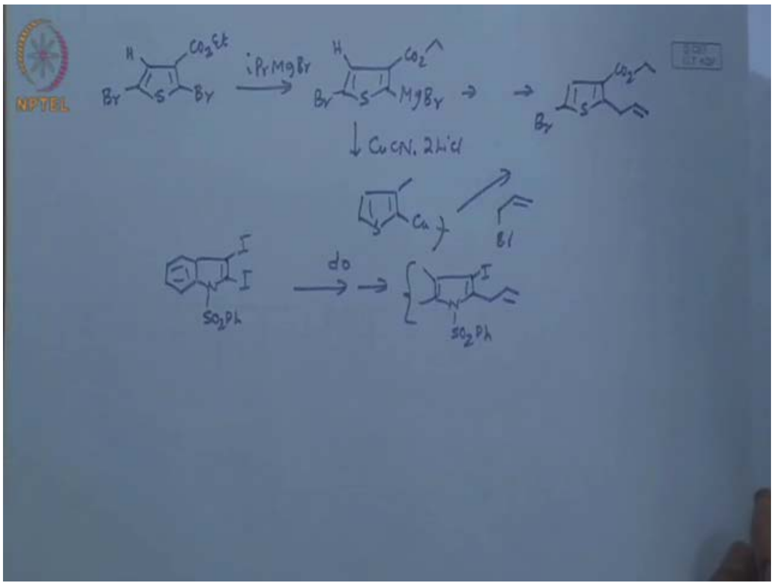

Now, let us this is an example which you give an lots of lessons actually, lessons here the starting is therafin again, if you recall in the previous class the therafin magnesium chloride was made by deprotonations. In these case isopropyl magnesium bromide, there is a possibility of deprotonations because, you have a hydrogen of here, and all these things. So, many thing can happen, it can take deprotonation, it can do the halogen exchange, it can do halogen exchange, it can attack the rest.

Because, in the school you have been learned oregano magnesium means, it will react with nestered, from the corresponding if you don't know are alcohols right. But, just by proper choice of oregano magnesium, in this case it is little bulkier. So, you are rather directing the group that protonation and halogen exchange, protonation exchange, deprotonation and halogen exchange are often competing with each other, in terms of lids. So, know and you can guess, which one is likely to be removed since this hydrogen is iron from sulphur.

So, these it is not very favorable one. So, between the two bowing then, the steric bulk has prevented, it is reactions with the s l group and then halogen exchange. And now, which halogen, just a guess because, it is a function start of carbon M and function of carbon M. So, you have an electro doing groups here, estern, so it is likely that this is, this being removed and you can get transmutation. Now, I want wanted to say elaborate this one because, bonding allied substituted compound, so what would be your choice.

If you did not know anything, you have done just co institutes allied bromide, but that’s this lot of complications. As I told you once before, the oregano magnesium are good in certain cases they are very complicated that direct, that is the genesis of kumada coupling. Why kumada coupling was required because, strek reactions of the oregano magnesium with the alkulating agent are not very step forward. And because, of many problems one of these problem again not transmutation, this is again at transmutation, this is halide sorry do not transmitalated, halogen exchange can takes place depending on their marginal decayed differences.

So, what would be next step then, you want to get this one. So, what should we do, in the moderate the reactivity or change the reactivity. So, how do moderate the reactivity go to the transmutations, so the commonest agent for transmutations because, normally when you go think about transmutations, we should first think about non transition metals. But, if you have magnesium then of course, there is alert if you have go to transition metals. Then once, you go to there then you have find some what cheaper and q plus cyanide is cheaper and 2 lithium chloride.

Lithium chloride actually, provide solubility q plus cyanides this agent should be soluble partly in organic solvent. So, once you have these then, so you have now q plus cyanide and eventually you get this copper plates, oregano copper I mean. And now the reactions smoothly proceeds, to get this compound. So, this is a nice example actually, it gives you a different way of making is these and that and this. So, like wise, exactly say for example, you want to apply this sequence to in dole chemistry, you take an protected indole, and dyandoindole.

So, you apply the same sequence the same sequence as have up, so what do we expect, now you have a options selectivity. So, you have two different iodine’s now, you know which one, the one next to the nitrogen and, we will get to the product. So; that means, one iodine can be selectively and let us take one or two more many example from this 6 membering systems.

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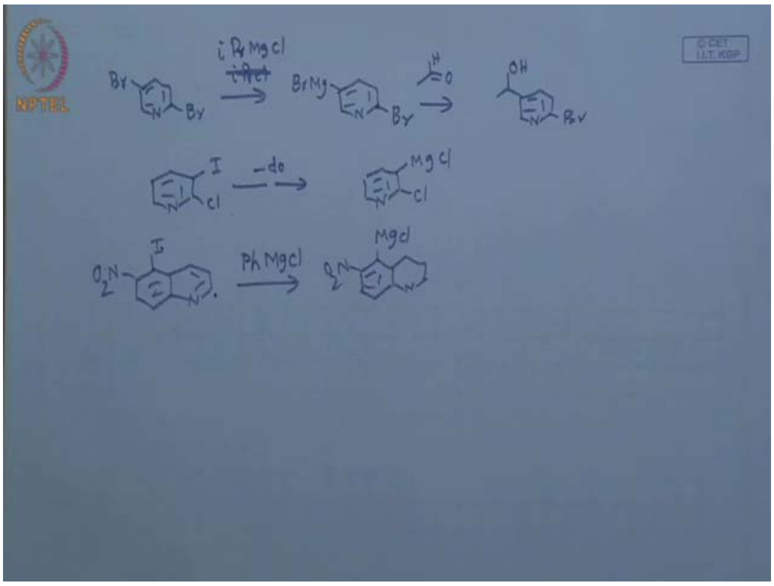

This is some thing, which I could not explain probably you will be able to explain; that means, there are some result, which cannot be explained. Once again, isopropyl chloride sorry isopropyl magnesium chloride. So, what do you expect, what do you expect from this reaction, while one thing you can say that unlike beetel lithium, remember chichibabin reaction, that is a possibility of chichibabin reaction, but again beetel lithium, peenal lthium there more nuecrofolic than corresponding. So, we cannot expect chichibabin kind of reactions here.

So, then; obviously, halogen exchange possibility, there is a possibility. Now, which halogen that’s what I thought, the some may be we have to invoke something else, but in this case reaction has taking place on the other halogen I don’t know. Then if you do this all these reactions are sent now, if you react with stelldihide. So, a new c c bond to be formed c c bond typical of gridner reactions, so will hard this. And one more example, probably again a pyramid case now, you have iodine and chlorine if you do in this previously agent.

So, what do we expect and now this little complicated. In the previous case both are bromine, but in this case one is iodine and one is bromine so; that means, bond strengthening as well as acidity etc. But, like before this iodine is root and you get the magnesium chloride, may we will take one more few system, this is example where you have iodine and nitro, this is special example may be time permits will talk about little bits of these things.

Oregano magnesium compound towards the nitro compounds and this case, this example requires phenyl magnesium chloride, then the special kind of reaction we will talking about probably towards the end of the class, may be or in the next class. What you can see there are once again, so many possibilities nuclifere addition to this two positions here. Then addition elimination can takes place, you have add compound in case of payroll if you have seen chlorine, undergoes addition elimination then essentially displacevely s p 2 halogens.

So, there is a possibility and also you have note take of the other possibility, the other possibilities is halogen exchange, between the addition and elimination halogen exchange is also a possibility. It depends on the reactivity of organic wave not, the wave not is could reactive, then it is likely to get you can get this halogen exchange system.

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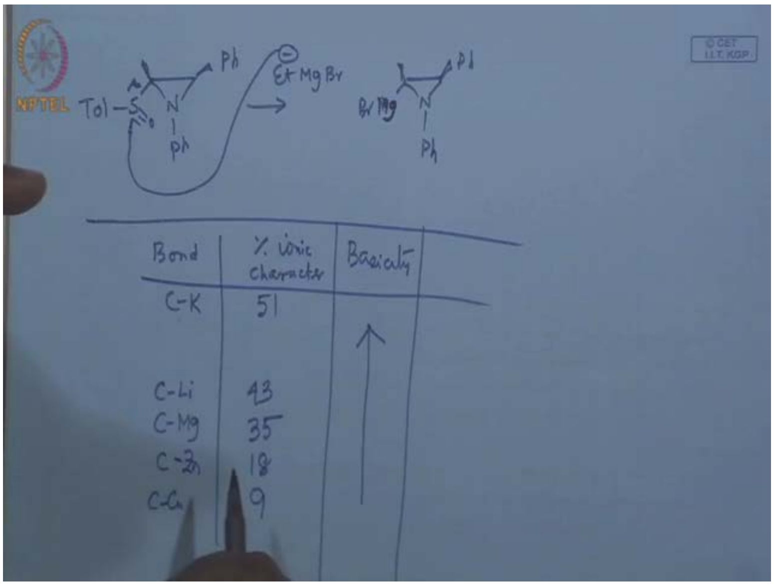

Bond	% ionic Character	Basicity
C-K	51	↑
C-Li	43	
C-Mg	35	
C-Zn	18	
C-Cu	9	

And this could be I have a special reaction only for saturated hetero cyclic this could be useful for oriset, ((Refer Time: 41:16)) you have now, this is sulfoxide and a phenyl

((Refer Time: 41:29)). Now, if you use ethyl magnesium bromide, let us see what could be the possibility, what reaction do you expect at should be opening, why should we open, no even before using this also has strength. So, in coming contact this an strength an increase right.

Fundamentally if you see, organic reactions are not many addition, substitution, elimination and these things all few organic reactions. So, why not addition, so actually in this example this is typical example here, it attracts the sulphoxide, it forms a magnesium reagent, magnesium bromide, by sowing the bonds here I mean to say ((Refer Time: 42:45)).

So, bromide and this is magnesium, so this is actually also the nice way of making corresponding carbon iron; that means, sulphoxiode can be used as carbon iron source. And, so for we have talk very quickly I will just give you this very important guideline by the way. So, the bonds in oregano metallic's normally are classified, I mean in several kinds and percentage unique character example.

So, in oregano metallic chemistry we talked about, let us lithium oregano lithium, percentage of unique character of oregano lithium could be how much, any idea, really how did you know, just interesting you remember it, that's great exactly 43 that's real. Then you have to tell me this one, then I will then what about potassium, while it is 51 then other extreme copper is 9. Now, you can fill in the blanks right, now you can fill in the blanks this gives you some idea, what does it tell you, if you have organo potassium that becomes more I will say bacicity how is that, bacicity.

Bacicity, goes up in this direction or all of us know bacicity has some resembles with the nueocrofilicity. So, if you have potassium salt that becomes more nueocrofilicity, so similarly, why should magnesium fit in on the top or below good. So, how much is it, that's interesting, this is here gambling or not good 35 very right, that is great. So, like these you know rank them, but for us the numbers are not important, numbers are the to ask the important in the order. So, if anybody come across the based of slosses base.

What is it munmun, you nodded your head, what is it fourthier talked about, slosses base is beetel lithium and potassium ((Refer Time: 45:40)) what does it do, it just exchange the metals, so becomes carbon potassium bond. So, becomes more nucrofilic more basic one of the strongest base in organic chemistry. So, this order is a very useful one, then what we do proof then oregano zinc because, today's topic was oregano zinc.

Here, below magnesium; that means, below magnesium now, should be the tell me what is the value, across 18. So, you see there is a dramatic difference between the oregano magnesium and oregano zinc, what is what does it tell you, oregano zinc is less reactive then. So, that is why they do not react with oregano zinc do not react with asters and that is the origin of refer mercury axis, but if you want to s p 2 horizon, s p 2 zinc how do you make, how do you produce it.

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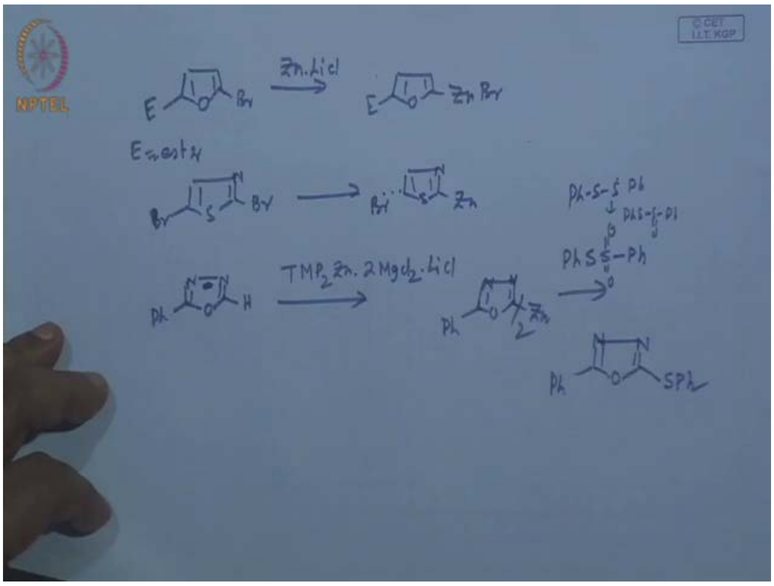

And in case of brittle cycles, if you have E transfer here right, if you have brovin equal straight way use zinc, straight way zinc and with the lithium chloride, apparently this x is preceding of an the reactions, you can straight way produce the corresponding zinc compounds. So, take any other phi member hydro cycle, within thyozole for example, bromine now, to bromines. Now, zinc could be organizing could be produced, again now in this case have the options right.

The bromine there are two different kinds of bromine, the one digits more level and we know which one is more level because, one between the two hydro atoms and, so zinc is plus here, and the rest of the things. And then react with the device is quite similar, required and then also there are reactions there are reactions actually, by which one can do the zincation by direct d proportion, direct d proportions. For example, in this k is a 5 numbering sorry ((Refer Time: 48:02)) well derivative and we radian here nitrate hydrogen here.

So, you want to do the d proportion here, I mean you have stop the nuclear addition. So, what you do, this is elision regent TMP all of us know heard the term per perpedial, 2 and then zinc, they may be all kinds of recipies or all kinds of the recipies 2 magnesiums this is nokial, this is actually nokial agents. Magnesium chloride and what else one more apt to be there lithium chloride. So, anybody can guess now, actually lithium chloride has a remarkable evil day I do not know, I am unable to actually find the real literature original literature.

But, people say lithium chloride has lot of a advantages, lot of a important reactivity profiles, we have to regard that, if anybody we can just take special interested lithium produce useful additives in organic chemistry any case. So, then you got these; obviously, zing case and done right and then this zinc case and reactions all possible reactions one can do it.