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

Lecture -10
Oxidation in Heterocyclic Chemistry

Before we take up this today's topic that is Oxidation in Heterocyclic Chemistry, we will go back little bit, and try to solve the problem we gave you last time, I do not know how many of you have worked out, how many? There are two kinds of problems; one is to unite two aromatic units I guess, two aromatic unit or one aromatic units or two aromatic it is, anybody of you have done it, it is just sort of somewhat equivalent to a weak area substitution reaction.

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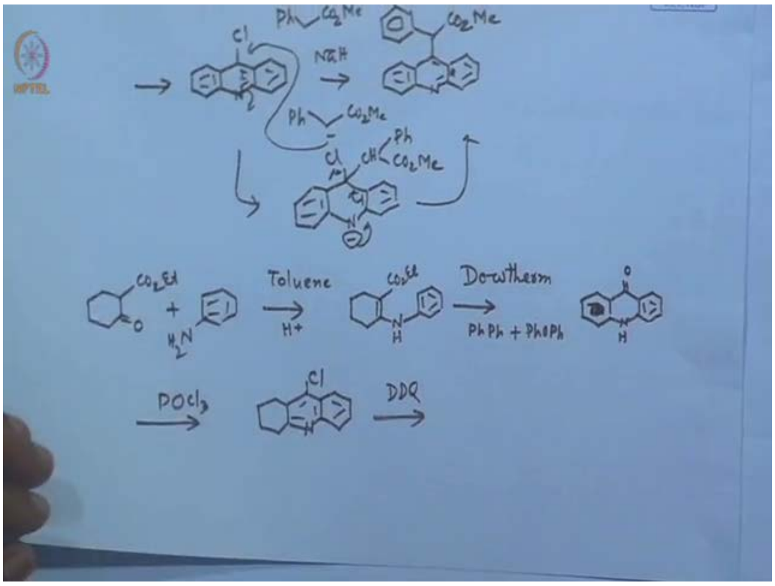

That was a reaction between a molecule of this kind, when I say molecule of this kind we should not talk about this kind, we have to tell the specific name. By now all of us know what is the name of this nucleus, what is the name of the nucleus? Quickly.

Student: acridine.

Good, acridine. So, if you have these and then I think we have to make a compound where you will have this acridine nucleus, and then you have to substitute I guess, sorry, this is ester unit with a let us say, with an aromatic unit.

So quite obviously, and the reaction makes any demands that in additional elimination is a process; additional elimination is a process for acridine nucleus with an ((Refer Time: 02:13)) groups at two position or four position. In this case that means what you have to do, you have to take the corresponding ester, that is it, corresponding ester and a base oxygen and sodium hydride works. And all of us know that these two together would give you corresponding amine here, and then amine goes to the carbon having chlorine.

So, an addition takes place so eventually what you will get, you will get sort of a reaction, which is remission of shift base, negative charge is reduced and what we have now, you will have an additional proton. So, Cl CH and then, phenyl and CO 2 methyl ester and what next, I think again we could like substitution reaction but in this case, you do not have to do that, we can straightway eliminate these. This is a typical like hanger reaction, this is hanger reaction so this is one of these way and how to get this acridine nucleus, is not that easy though.

But, in this case it is pretty easy, how to get these, this acridine nucleus and I will tell you there is something else, may be pretty similar to that for example, I give you also the problem that, if you have an ester of this kind and then, what is the next reactant, any name. So, what do you expect out of these, the reaction condition is in the say a toluene, reaction condition is toluene and normally for any sort of conditions or reactions with amine, acidity required not a base so paratoulene sulphuric acid.

So, what do you expect quickly, not really immediately what you would expect, inamine so what do you get is inamine and ester here. What next, this is your typical reactions in heterocyclic chemistry, ring closure so inamine also under strongly heating condition undergoes cyclic amide formation. If an ester and amine is sealed to heated together at high temperature gives corresponding amide. So similarly, it is in internal amide and in this case, a special kind of solvent is used called dithrom.

I do not know how many of you know, it is a chemical that is devised, that is sold by dow chemicals of USA. Now, you see it is a high volume liquid and this liquid can be boiled to around 400 degrees centigrade, that is highest temperature. That is, at 400 degrees centigrade it is liquid there are very few and it is a mixture of biphenyl, should basically be solvent plus the corresponding diphenyl ether, so it is a mixture of two chemicals, high volume solvent.

So, once you have these then, internal amide or phenyl fungus amide is formed and what you get is this, corresponding ketone. And what next and very similar, only one of the ring is not aromatic so if you treat this with standard, again with a PoCl 3, very standard chemical in heterocyclic chemistry. What you expect quick, what you expect, you expect this aromatized compound, it is sort of like acid chloride, it is standard protocol and this protocol is also used for making the analogues from quine analogues.

This antimeridial ((Refer Time: 06:39)) and all this and if you want to let us say, go to the acridine nucleus from here so what you have to do.

Student: ((Refer Time: 06:49))

No, that is the trouble, yes if I did not know, I would have also answered this question by saying DDQ but that is the reason the next topic is about. So, and why suddenly, we identified oxygen in heterocyclic is a separate topic because whatever we learnt about oxidation in standard organic chemistry, cannot be extrapolated to heterocyclic chemistry. Likewise, hetero atoms exert all kinds of special reactions, we have listed 12 different kind of reactions, also those hetero atoms all create problems.

It is not standard protocol that whatever you have learnt in organic chemistry, should be extrapolated and should be applicable to heterocyclic chemistry, the presence of lone pair itself can complicate the situation. So, for example, the case like if you want to try DDQ oxidation, there could be complication number 1. Number 2, since you are young, you should have a knowledge about the problem that DDQ is very expensive so you should find a substitute for DDQ, if you can find out.

There are quite few example, palladium carbon, selenium those are all very old but you have to have an new reagent that can cause dehydrogenation essence or aromatization, all these things. But, there are not many though, they are not many that is part of the today's topic so we will talk about it.

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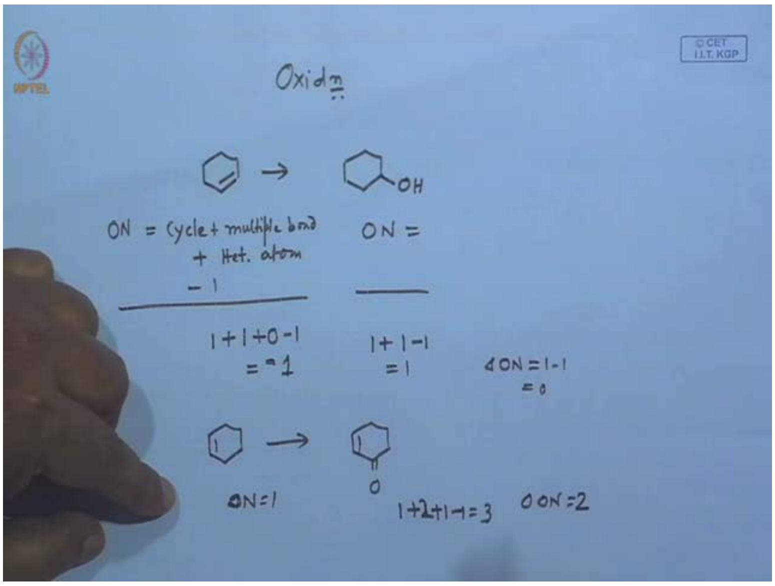

So, that means oxidation, oxidation is a problem in heterocyclic chemistry primarily, because of the presence of the lone pair and the presence of hetero atom. So, whenever we think of oxidation actually, we think of oxidation of alcohol with ketone, alcohol with the corrosive carboxylic acid and those things, all those things. But, when it comes to heterocyclic chemistry, you have to be a little cautious because the oxidation can take place at the nitrogen centre, hetero atom centre, in the neighboring centre, you know on to the nucleus and in addition, to the existing functional groups, etcetera.

So, you have many more options, many more things to be considered before you choose a right oxidant. So, before we come to these other details problems, let me just very quickly so many of you have attended my fourth year class so we will again talk about little bit for those who do not know finding oxidation. Normally in high school we say, oxidation means, addition of oxygen, removal of hydrogen or else one more definition loss of electron.

But, when it comes to organic chemistry, we have a quick formula, how to find out this oxidation number. And if you recall, let us say suppose, you want to, this is a very simple one though, in this case what do you see, if you just calculate with molecular formula and you see this, that there is a difference in addition of oxygen that is very quick. But, most often, the problems are not that simple, we have all different kinds of problems. Let us say, to make this a little tougher we are using oxidation or reduction let us say, we are talking about this one.

And you recall that, oxygen number given to a compound is determined by these oxidation number, number of cycle, number of multiple bond and number of hetero atom and then, minus 1. So similarly, in this case, you have oxidation number of this product could be same formula so this is the master formula and for the left hand side material, number of cycle is 1, number of multiple bond is 1, number of heteroatom is 0, minus 1 so number of heteroatom is 0, minus 1 so oxidation number of study material is 1.

Now, if you go to the right one so number of cycle is 1 and then, heteroatom is 1, no double bond, minus 1 and equal to 1. So, delta oxidation number 1, minus 1 is 0 that means, there is no change in oxidation number that means, this particular transformation does not require any oxidizing agent. That means, there is late oxidization taking place, this is one of the very simplest way of looking at it. But, when it comes to heterocyclic chemistry you have to add one more parameter, what is that?

Student: ((Refer Time: 12:05))

No, lone pair, lone pair of electron, actually this formula was given by somebody else from US then, I modified that for heterocyclic compounds. So, you have to add 1, I have published paper in journal of teaching organic chemistry long back in 1997, if you are interested you can go to my page and find the article there. And so what you do, you have to basically take care of the lone pairs that means, whatever in these atoms are added, plus number of hetero atoms.

This is not only a good formula for finding out, whether reaction is oxidation or reduction, it also tells you how many equivalent of oxidising and reducing agents would be required. For example, if you take let us say, if you have these cyclohexene, you are going to do from cyclohexane to cyclohexanone. So, what is the level of oxidation, how many electron oxidation is are required. So, for this cyclohexane, oxidation number is 1 and this cyclohexanone what it is oxidation number, 1 cycle, 2 double bond, 1 heteroatom, minus 1 so 3.

So, delta oxidation number is 2 that means, you need actually 4 electron oxidation , this is actually very good guideline actually. I mean, so far I have not seen an exception to this rule, if you have come across in fact, applicable to almost any kind of organic reason, if you come up with any exception, please let me know. And now, in the case of nitrogen, the problems are serious in heterocyclic chemistry, just I will just give you a background why it is so serious.

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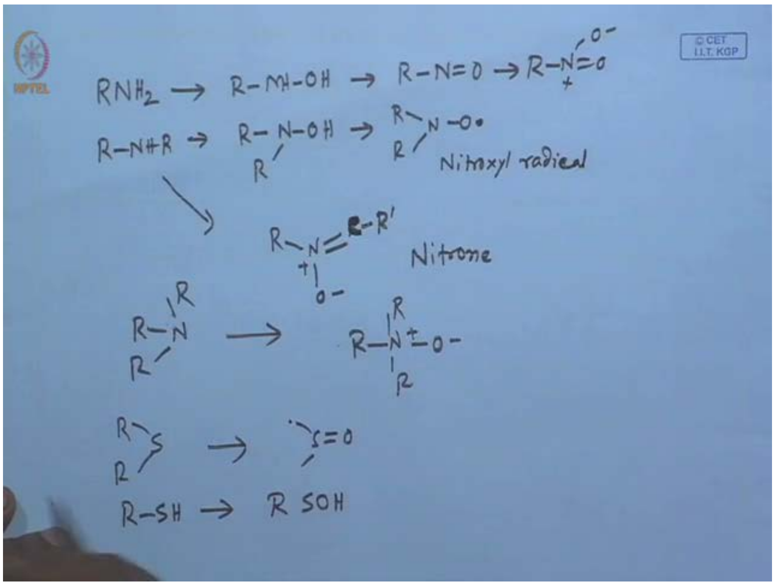

For example, if you have a primary amine so what is the next phase of oxidation primary amine, one can quickly say, it can go to hydroxyl amine. And this is standard one, if you want to further oxidize these then, further oxidize NO 2, these are typical one. Now, let us say, if you have a secondary amine, what do you expect in secondary amines, why you know, Ii can simply write these. What next, you have seen it, nitroxyl like in tempo maybe we will talk about today and this is known as nitroxyl radical like this.

I mean, you have all kinds of actually then, what else in fact, from these also, you can have oxidization, if you have a carbon here let us say, carbon here so you can go to these let us say, R prime now, this is carbon. What is it, you can from secondary amine straightaway go to the, you should know by now, what is this nitrone that is, you have so many varieties of these functional groups arising out of nitrogen. Then also, let us say if you have a tertiary amine, you should have an oxidation, what do you expect, inoxide.

So, inoxide that means, you have this multistute of functional goofs, which can be derived from these amines, this is only for nitrogen. Now, similarly, when you have sulphur compound, I think many of you know now, the next step is the disulphide then, you have sulfoxide, these are all old things then what next, sulfone. Similarly, when you have let say SH, it goes to SOH sulfenic acid then, 2 oxygen sulfenic acid, 3 oxygen sulfonic acid so like this you have all kinds of problems.

So, you have to be little careful but what we can say that, it is very difficult to predict a right oxidation agent for heterocyclic chemistry, it comes through experience, it comes with a little culture of chemistry. So, we will have more and more examples, just to justify that under variety of situation where, oxidising agent could be most appropriate, let us take a simple example, which is really unpredictable.

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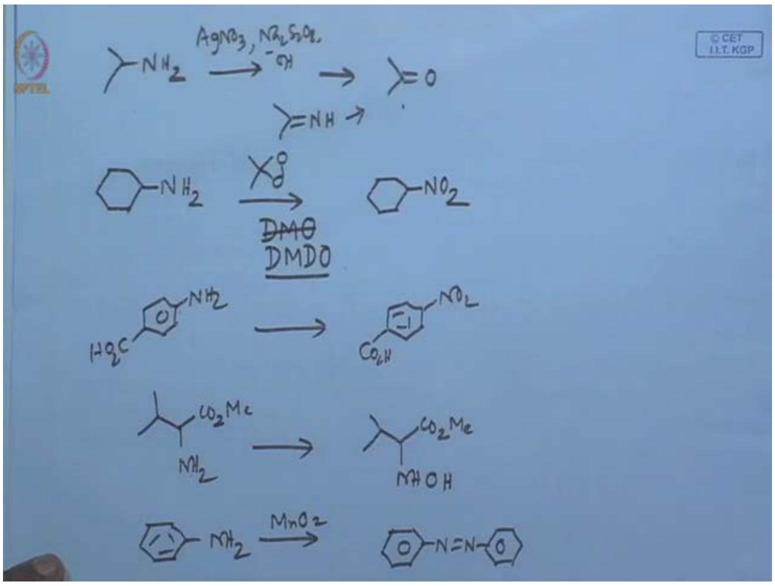

It is a primary amine, how to convert these into this?

Student: ((Refer Time: 17:58))

Titanium…

Student: ((Refer Time: 18:01))

So, let us see first, whether it is an oxidation reaction or not, I think a little obvious, somewhat obvious because nitrogen takes place of oxygen. So, oxidation number remains the same, you have a double bond, etcetera so oxidation there is that is all. So, if you are very strong in bioorganic chemistry, you can quickly say how to oxidize these, who knows. In bioorganic chemistry, there is very famous reaction starts with the name oxidative.

Student: ((Refer Time: 18:50))

Oxidative deamination so that is a perfect law so if you form a shift base isomerized hydrolized so then, just oxygen gets transferred to the essence just seen as, but in this case, if you do not want to do it chemically as I said before, somewhat unpredictable. But, like silver nitrate and sodium perodisulphate and alkaline medium, how do you come up with these, absolutely no idea, it comes with experience, it comes with the findings and from literature, there is no way one can directly do with so what eventually get basically, dehydrogenation takes place.

If you recall, in the last class I talked about that alpha radicals, alpha to nitrogen, alpha to carbonium ion and then, these carbenes they are all stabilized by nitrogen. So, that is the driving force, why this hydrogen is transferred to oxidizing agent and forms these NH. And once this NH phase is formed, there is a likelihood, that this should undergo water or alkaline medium, it goes to the corresponding ketone. But, in general, it is of very simple essence and certain cases, they are permissible.

Now, I take up a very similar molecule, just consider a simple molecule let us say, this one, this basically gives you an idea, silver nitrate potassium perodisulphate could be an oxidizing agent and compatible heterocyclic compounds. Likewise, there is another oxidising agent, many of you probably are not familiar with but they are very famous oxidising agent, which comes from acetone and oxsone, anybody knows. Again I think, I have informed the 4 th year, I talked a little bit about this oxsone, it is famous.

In my lab we have, potassium monopersulfate, potassium hydrogen sulphate and potassium sulphate, it is a tri-salt mixture. But, the active component is potassium monopersulfate KHSO 5 caro's acid, corresponding salt of the caro's acid. So, if you mix with acetone, it gives you nice product which could be distillable but it is not commercially available. Whenever it is required, you can make it in the lab and then, convert these, this is nothing but additional heterocycle.

What is it, I think the nickname is this dimethyl dioxydant, very clean oxidising agent and many times it gives nice clean products. So, let us say, in this particular example, what do you expect then, I mean all these possibilities are there, all this possibility it confirms amine, it confirms the anoxide, it confirms this hydroxide amine, it confirms the nitro all these things. But, it is such a powerful oxidising agent, it straightway that means, this will give you just some idea, that it is a very powerful oxidising agent, it gives the corresponding nitro compound.

Likewise many of you have studied this before, let us say anthranilic acid and same product and if you are given to convert these into corresponding NO 2 and the carbocyclic acid, often what we do, we do ((Refer Time: 22:50)) something like that. But, in this case, it is perfectly all right now, one can also suggest that let us say, potassium peramanganate but potassium peramanganatewill give you all kinds of things.

What are the things, if you have aromatic amine, potassium peramanganate will give the corresponding nitro nitroso and then, azo compound diamerize, hydoxy compound all kinds of things. So that means, nitrogen actually makes the situation very complicated unless and until you know these oxidation rightly. Like let us say, this is again something quite unlikely, this is aliphatic amine, that is similar to this. If you try to do oxidized in analogy the previous one, one would expect that the reaction will give you the corresponding NO 2.

But, actually, the reaction can be interrupted at this stage, hydroxyl amine, often you know when asked how do you make hydroxyl amine now, people start with nitro compound. Nitro compound and ((Refer Time: 24:01)) agent will you the… Very similar but mind it milker merger cannot take place in acidic medium, it will straightaway go to the corresponding NH 2 so all these problems are there. Like say, this is a very important topic, important oxidising agent let us say, instead of potassium peramanganate if you begin with amino 2 let us see, you have read this in B.Sc.

Student: ((Refer Time: 24:40))

No, B.Sc you have read, I can still vividly remember Finersmoog on the left hand side, that I remember. Benzoquinone, easy but also, the same reagent can give, what is this, what is the name of the molecule, azobenzene, it is not diabenzene, 2 nitrogen only this azobenzene.

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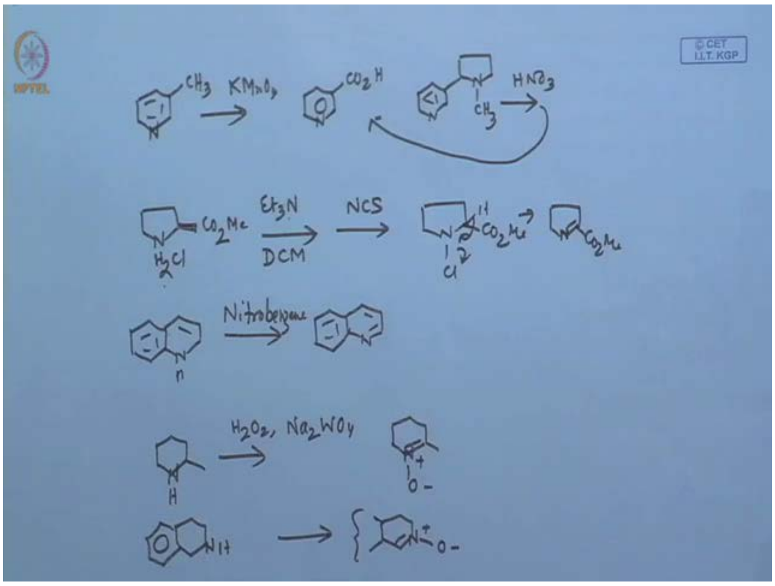

let us look at the contrasting behaviour of potassium peramanganate let us say, you have 3 methyl pyridine. Now, you want to oxidize these two corresponding carboxylic acid, I think all of us would be able to give the right answer, what is the reagent?

Student: Potassium Permagnate.

Very good potassium peramanganate, very safe reaction in the sense, that the nucleus is deactivated, is not subject to oxidation with a strong reagent so side chain is oxidized in analogy with benzene chemistry. Now, let us take up another molecule, I think it is very similar again it is a substituted molecule but in this case, the reagent is this one, many of you know the nucleus is nicotine nucleus. Now, I do not give you the product, you tell me the product and if I say let us say, treat these with HNO 3, what do you expect.

Now, things are little more complicated think about it, it has aromatic nucleus, it has aliphatic nucleus, it has an aromatic nitrogen, you have a non aromatic nitrogen and this thing but the reagent as nitric acid. So, the first thing that has to take place is protonation of both the nitrogen, that is perfectly all right but also, together we know that, nitric acid is a very strong oxidizing agent. So, it will oxidize it and it can chew up the whole molecules to burn it or you can give it a nice clean product. To give you the answer, it gives you a clean product.

Student: ((Refer Time: 27:09))

That could be the first yes, what he said is perfectly all right, actually double bond could be there let us say, further oxidizes, it is a powerful oxidizing agent actually it goes to this one. So that means, the aromatic nucleus is so deactivated, only this aliphatic portion is... so it is a side chain, just like toluenic acid, benzenic acid. And quite similar to that, this is not let us say, somewhat it is not purely oxidizing agent, let us say you have chlorine hydrochlorides now, I acted these with triethylamine and DCM that is, dichloromethane.

And what are the residues obtained, it is treated with NCS, NCS stands for N Chloro Succinamide. So, what you expect, see N chloro succinamide also is an equivalent to oxidizing agent, it is a chloro diamine, bromium, chlorine all these things towards the right top corner of the periodic table, all these atoms and reagents are oxidizing agents. So, what do you expect basically, triethylamine obstruct the HCl present in this, it is a salt hydrochlorides salt so makes it freeprolene ester. Thereafter, you treat that with NCl so what is the first reaction you expect?

Student: NCl.

NC l, very good that is it so once you know the product is NCS, that is it and this is not stable one, you can guess why because you have a conjugation tool to be applied. So, it gives you the corresponding 6 base, if you look at this starting material and the product, difference is basically hydrogenation. So, it is again that means, this is actually an example to show that, in chloro succinimide could be a dehydrogenic agent or oxidizing agent.

And you have all I mean, just you all just little bit of the recollection, some of them are the recollections for example, if you treat these molecules dihydrokanolone and you want to do dehydrogenation. It is a serious problem though two corresponding kanolene and you all know the answer though like DDQ would not be a viable answer reason being, kanolene is so cheap. Kanolene let us say, 1 liter maybe 500 but required DDQ per 10 grams or 100 grams DDQ could be costing you 10000 rupees.

So, DDQ is not the right answer for this kind of transformations any suggestion, there are many oxidizing agents which often we did not think about the...

Student: Nitric acid.

Nitric acid, you can understand you know, nitric acid is not a good one, see this is the thing you have to think over. Now, at this stage, making a good choice of oxidizing and reducing agent, whatever the reagent in the organization is, is tough especially, when you have a hetero atom. See, nitric acid all of us know, nitric acid can cleave the carbon carbon double bond like cyclohexane converted to adipic acid, have you seen the experiment done before, anywhere in lab.

Just boil nitric acid, put cyclohexane or cyclohexanol or cyclohexane all of these chemicals will be converted into… in no time, in 10, 15 minutes to corresponding nites, crystalline solid of adipic acid. So, such a strong acid actually, strong oxidizing agent so you cannot think of, not only that, many of us know anidine. Anidine undergoes very facile nitrogen so it is equivalent to anidine actually, it can lead to nitrated product, nitric acid would not be a good choice for this sort of oxidation so…

Student: Pyridium carbon.

Pyridium carbon, that should be all right but I will give you an example where, pyridium also diverts the reaction into other directions. But, the best thing would be, if you recall a reaction which you have studied in B.Sc where, you putting nitro benzene.

Student: ((Refer Time: 32:17))

No.

Student: As a solvent.

Right, not as a solvent, that is also a reagent, ((Refer Time: 32:30)) so let us say, this is something different and this is very useful these days. Let us say, you have a secondary amine, basically by giving these examples, I am trying to show you some of these usefulness as well as in the limitations. For example, if you take hydrogen peroxide and secondary amine, what are the products I have already told you, first it goes to hydroxyl aamine then, next this nitrone.

So, in this case, if you take sodium tungsten it will nicely give the corresponding nitrone similarly, take isokanolene, it goes to corresponding nitrone. So that means, this hydrogen peroxide might be hydrogen peroxide, secondary amine, it is a nice combination and sodium tungsten is a catalyst basically. Your stoichiometric oxidizing agent in hydrogen peroxide, it will straightaway give you the nitrogen, it is a nice impression of the nitrone.

And reactions are there but basic oxidizing agent is hydrogen peroxide and often sodium tungsten is replaced by hydrotelside, it is basically a silicate kind of catalyst.

Student: ((Refer Time: 34:12))

Nitrogen after reduction gets nitrosobenzene, now again let us say, probably we also to have in our mind a possible oxidizing agent.

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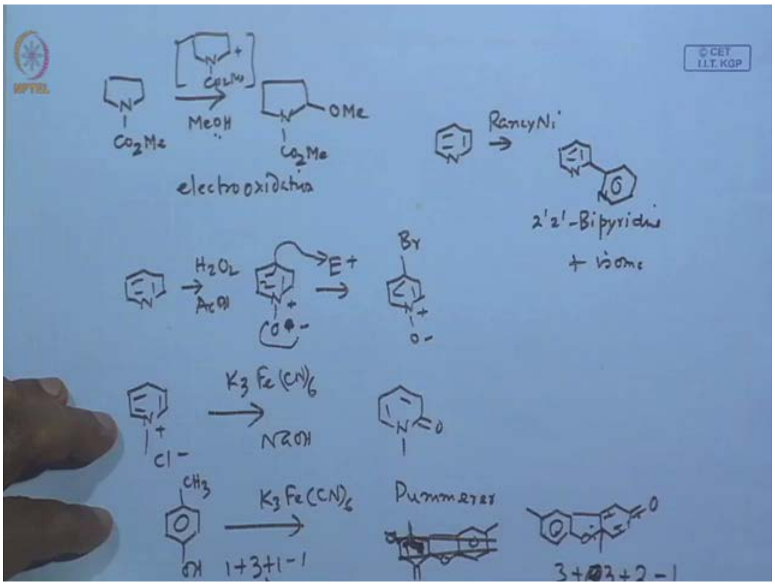

Often we do not deal with or we do not talk about it let us say that, methanol then, it can be converted into corresponding this methoxyl compound. It is very easy that means, alpha position can be substituted by methoxine, again due to the lone pair effect, the lone pair of nitrogen can stabilise the corresponding carbonic atom, etcetera and oxygen has a lone pair. So, what do you expect that, there must be a some sort of carbo carton here that means, hydrogen should be removed from there and how do you do, there are plenty of oxidizing agents, one of them many of you probably heard of CAN, anybody knows.

STUDENT: Ceric Ammoonium Nitrate.

Very good ceric ammonium nitrate, it is a very famous reagent for oxidizing dimethicone, benzene toquinone and also for the oxidation of alpha position sub nitrogen that is it. But, obviously you have lots of wastage but one of the most successful green chemistry oxidation is electrochemistry, electro oxidation, anodic oxidation. Electro oxidation, electro oxidation here a very important step in organic chemistry I mean, often we do not deal with, reaction takes place reaction are very clean and it is often used by Japanese chemistry, they are very fond of electrochemistry.

So, many many synthetic processes in fact, I heard I do not know had never went to there is a place called ((Refer Time: 36:26)) in West Bengal, not you, that used to be a factory actually, be used to reduce nitro benzene to corresponding aniline by electrochemically, that is what I heard of, never been to that place. That means, many many simple reductions can be carried out electrochemically, if the reaction takes place process are very simple.

Many of you probably do not know the voltage requirement is very little less than 10 volts is enough for all these organic transformations and polymer industry also electro polymerization is very useful. So, in this case, what you get is a nice functionalization at a particular position and this material has been used for many synthesis. And then, this is another example, maybe we can talk about, this is also a synthetic challenge. Now, let us say, if you take Raney nickel and simply heat it, what you expect, Raney nickel should be an oxidizing agent or reducing agent?

Student: ((Refer Time: 37:43))

It should be…

Student: ((Refer Time: 37:47))

No, palladium alone is an oxidizing agent, pyridine in combination with hydrogen is a reducing agent, so you have to be a little careful. So, actually, this is the way this can be dehydrogenated 2 2 prime bipyridine, this is how it is made but the yield is very poor less than 50 percent for sure. And of course, the isomer this 2 2 prime, 4 prime, 4 4 prime all these things are there. But, there is no simple solution, I you just look out this molecule, the ((Refer Time: 38:34)), people have used it but again, they do the cross coupling reactions.

So, cross coupling reaction would require pyridine and then, bromo particularly, at 2 position bromine is tough let us say, 2 bromo pyridine. How do you make 2 bromo pyridine typically, you cannot go by the electrifilic substitution reaction or neutrifilic substitution reaction. 2 bromo pyridine, how do you make?

Student: ((Refer Time: 39:00))

No, idea is good but when you form inoxide then, most of the electronic substitution takes place at full position. So, I do not have to teach much of this pyridine before position but then, see the whole problem is that, you have to remove oxygen.

Student: ((Refer Time: 39:26))

No, mechanistically oxygen is not removed during the oxidation.

Student: ((Refer Time: 39:37))

You consolidate the literature basically, when you form an inoxide, since we have been talking about, this is again that this is again oxidation kind of reaction. Like, if you use hydrogen peroxide what happens, inoxide is formed normally, acidic acid is given it forms para acetic acid and then, this. And then, if you try the electrophylic substitution reaction and often this electronphylic substitution reaction takes place at four position.

So, if you do bromination so it is likely nothing happens to the oxygen, instead he will get four bromine anoxide then, use a low valent phosphorus oxychloride and then, it comes out as oxychloride or whatever. So that means, you have so many steps and then, you do this cross coupling so this reason is very expensive, bipyridine unites complexitic agent in polymer chemistry. So, this is a tough problem, if you can come up with right solution and it should be publishable, just produce biphenyl directly in single step and more than 50 percent I can guarantee you that, this is publishable result.

I mean, what I am trying to say, some of the problems in heterocyclic chemistry are existing today. I mean, there are quite a few and then, let us say and this is another quite often noted, let us say you have a pyridium chloride, how do you know you are dealing with salt. Most of the heterocyclic are salt because of the nitrogen, in this case you do silver nitrate test that is quite easy. If you are handling an unknown compound, whether methyl is there, too many methyls here and there, that thing is quite tough.

I mean, in the earlier literature what people used to do reaction with potassium ferricyanide and then, a little bit of sodium hydroxide. So, what do you expect, what you expect again is nice reaction though, that is how actually the nicotine compound was isolated. The structure of nicotine was established, you get a piridone that means, potassium ferricyanide is an oxidizing agent, there are cases there are plenty of cases where you could do.

So, at the moment, there are quite a few, may be one oxygen can take this potassium hydroxide and the use of potassium ferricyanide in mixing this, these days people are using potassium ferricyanide for synacthen reaction. If you have halobenzene, etcetera you can substitute the halogen by cyanite using potassium ferricyanide, not potassium cyanide. There are other oxidative dimerization for example, I am almost sure, I will manipulate a little alkaloid.

Let us say, for example, use paracrisol and potassium ferricyanide so what do you expect let us say, just a guess phenol, any guess. Now, we know that potassium ferricyanide is an oxidizing agent, where is it used, largely used in a very popular reagent, hints, oxidation, alkene chemistry, surplus what else I have given you everything, all the details. Read ((Refer Time: 44:15)) actually, this hydroxidation process is potassium osmate and the stretching amount is potassium ferricyanide, co oxygen, these are the things you have to remember.

To have good organic chemistry you have to remember these things in fact, we are getting older forgetting lots of things, this is something different, this is as I said. I roughly remember this example, if you find any mistake let me know presumably it gives sometimes, let us say pummerer ketone, not the pummerer reagent or the palmerrer rearrangement. Actually it gives you something like this, close trying to get a thing something like this let me see, I am trying to something like this is formed, mainly I have a little difficulty, one of the things is aromatic I know, the other is probably, now I got it, now this is called pummerer ketone.

So, if you look at, we can just quickly find out it is oxidization or reduction, how do I know, it is a dimer.

Student: ((Refer Time: 46:30))

That is ok but you never know quinone means, it cannot be oxidizing agent but the other side will be reduced. Cyclization taking place so cyclisation is forming dehydrogenation is taking place so again just basically, calculate that, that will be a very nice way of looking at it. What is the oxidizing number of this molecule, 1 cycle 1, 3 double bond and 1 heteroatom minus 1 so it should be 4, 1 cycle 3 double bonds 1 heteroatom, 4.

So, two of the molecules have been united from the atom balancing that means, total number of oxidation number is, in this case is 8, two times four equal to 8. Now, look at this molecule, how many cycles, 1 2 3, how many double bonds 4 5 6 7 and…

Student: ((Refer Time: 47:32))

4 5 6 and 7, this is 3 so this is 3 and 3 is 6, 2 heteroatom 1 and 2, we have ignored alter both of them so minus 1, it is now 10. So, it is 6, 7 is something wrong, no this is 4 and 5, cycle 6 minus 1. Aromatic ring means 4, three double bonds and one ring 4, 5 minus 1, 4 and the 2 molecules so 8. In this case, how many, 1 2 3, 3 cycle and 3 double bond here 4 5 6 also so this is actually 6, actually 6 double bonds, 2 heteroatoms minus 1 so it is 10 so it is a clear case of 4 electron oxidation. So, any case, this is a nice example and it is called oxidization dimerization and let us give you one more example.

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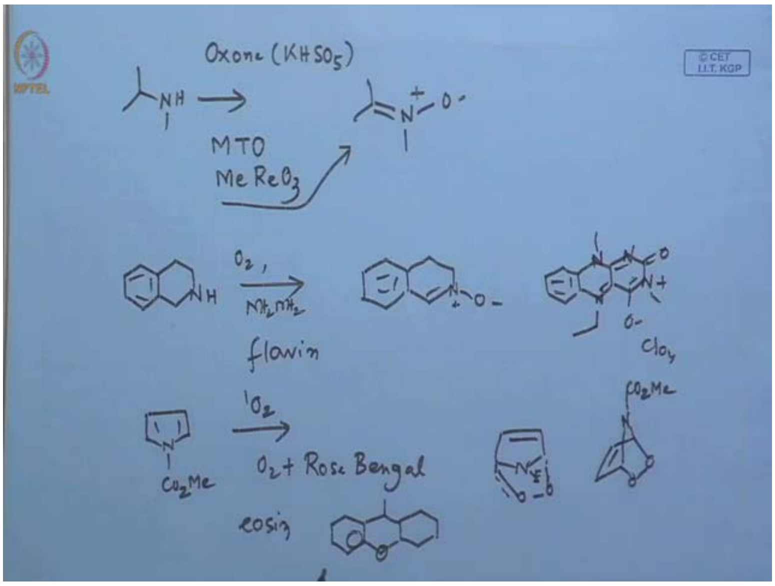

That means, this is just, this is secondary amine now, you can use oxone now, you know what is oxone, oxone is potassium monoparsulfate. And this is active component and other potassium salt so again I mean, this is quite difficult to predict what is the final product, the final product depends on the power of the oxidization. We can go for electrochemical series, etcetera all these things but in organic chemistry, they are of no importance especially, when you are singly evaluating chemist, you just have a rough idea about which one is more powerful oxidant, which is more specific towards nitrogen.

Had it been specific towards nitrogen, it will oxidize hydroxyl amine and this is further oxidizing agent then, it goes to nitrone. In this case, that is it I mean, it just absolutely no idea, it gives you the nitrone so previously, nitrone was prepared by hydrogen peroxide and sodium tungsten, here is oxidization. And there is another nice clean oxidizing agent, I do not know whether if you know or not MTO, MTO is Methyl renate just like oxygen tetroxide.

In this case, this is a nice oxidizing agent, this is to show that in heterocyclic chemistry, MTO is also useful. And then, other thing I guess, we will ignore small things probably, I will give you one more important thing here that is oxygen, oxygen is a terminal oxygen. Suppose, you have a heterocyclic of this kind, you treat this and you are likely to get and there are many more methods you have seen it. But, this can also be oxidized by oxygen, just oxygen and in combination with, I really do not know the use of this hydrogen.

Hydrogen is added and then, what is this, flavin so flavin is of course, an oxidizing agent a heterocyclic molecule so this is biooxidization chemistry by Murahasi. A Japanese scientist, Murahasi is quite famous for it and by now, probably, you know the structure of flavins, what is the structure, someone?

Student: There are quinine type but nitrogen.

No now, we are in heterocyclic compound class so we will go by heterocyclic nucleus, flavin is something like of course, it is a tricyclic first you have to say. Then, the two nitrogens are up here and this thing is aromatic, what else you see then, the other to nitrogens are in 1 3 position, that is it. The rest is basically what you said is like a quinone kind of structure and then, the rest of the things I would also not know. Since I have a note here, you can say this plus and this, and parchloride, this is a nice actually oxidizing agent here.

So, what do you see, simple oxygen can be used like the another example probably, you have to know. I think I will give you one more example, very similar, oxygen is an oxidizing agent in heterocyclic chemistry and let us say, it is a spiral nucleus, how to break this nucleus and to do so one can quickly draw the singlet oxygen, we have produce in our lab, it is pretty easy to produce singlet oxygen. The regular oxygen is inert, all of us know but how to make singlet oxygen, I think I have told you before in 4 th year again, the recapitulate…

Student: Rose Bengal.

Rose Bengal and similar molecule one more di, commercially available oxygen plus rose Bengal all of us know, the name originates from Bengal. Because, Bengali women used use vermillion, [FL] 4 th year [FL] actually, we should know, being Bengali we should know. But, the manufacturer is from Germany, German manufacturer made this then, to make it popular, they gave the name rose Bengal. It is basically xanthene dye, xanthene dye is also a heterocyclic one, what is xanthene quick, xanthenes again a tetracyclic just like pummererkitone or pummererkitone so you have this xanthene and other thing.

So, you have a phenyl ring here then, halogen in this case bromine, etcetera or else, I think we used eosin, it is a very similar dye, singlet oxygen has a typical pattern of reaction. Normally, it can undergo two different kinds of reactions in organic chemistry, one is in reaction, the other is the solar reaction. In this case, because of presence of carboxyl ester, it would undergo the solar reaction and the molecule that you get is this. So, this nitrogen will have the ester group E and double bond or else, one can just e clear quickly write this way.

So now, this is a process of oxidative dearomatization here, the molecule was the dearomatic. Now, it has been dearomatized, at the same time we have to introduce oxygen so oxidization has taken place exactly same. I mean, we will continue little bit with more of these oxidizations of the heterocyclic compounds, maybe we will also talk about a little bit of this.

We have quite a few more examples, I think we will probably take it up in the next class because it is useful process oxidisation and some of these selective oxidisation will also be taken up in the next class. Let me just quickly give you one more example, maybe like say in case of furan also.

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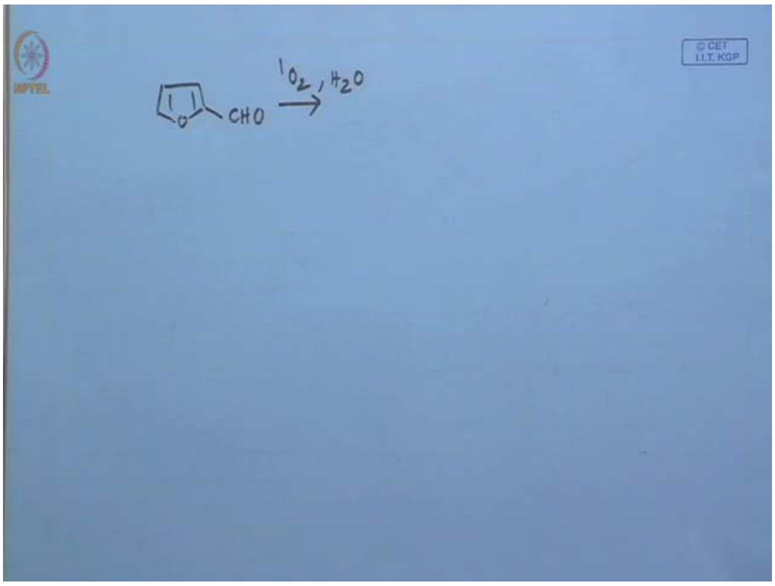

We also did one reaction phase for few run with singlet oxygen with water so the previous example was on pyrone and this is an example of furan. Furan also undergoes this addition singlet oxygen addition and try to figure out the structure of the product. So, we will have quite a few more examples in the next class on oxidation reactions.