Heterocyclic Chemistry

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Lecture - 11
Oxidation in Heterocyclic Chemistry (Contd)

Good morning. So, we will begin, we will continue with topic oxidation in heterocyclic chemistry and as you know this is very worst topic. Last class we summarized some of the important oxidizing agents and then used in heterocyclic chemistry and will continue the same topic because range of oxidizing agent use in heterocyclic chemistry is very big one. Today we talk about few task specific oxidizing agents.

What does it mean? It means some of these oxidizing only meant for a particular kind of oxidation and which include oxygen, hydrogen peroxide based oxidizing agents, brominating agents like bromine and n p s, then manganese dioxide, ruthenium dioxide or ruthenium tetroxide. Then i b x, all of us know what i b x is. Then we will also talk about oxiridine and then little bit of tempo tetramethyl piperidine oxides. So, this is in not sell list of the oxidizing agents will cover today and but to begin with. Of course, I will continue with the example we gave you last time.

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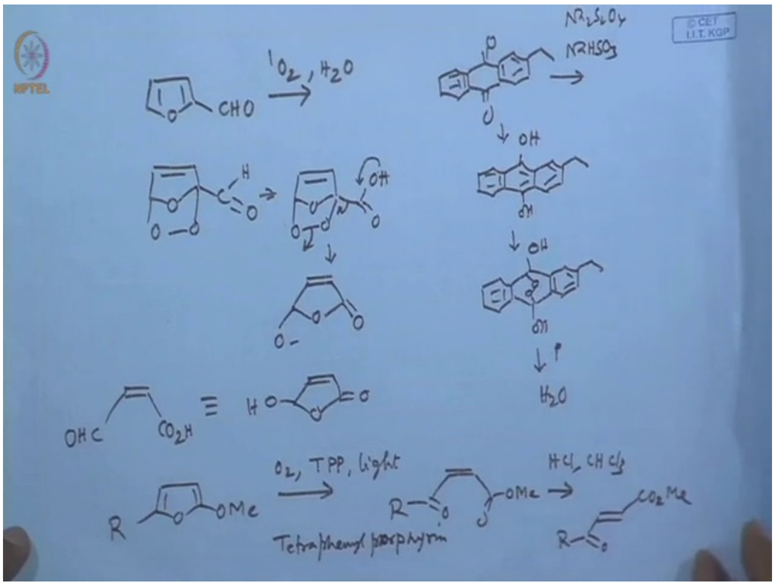

This is I think you have here, you can see for furan. For furan, in the presence of single oxygen and single oxygen is as I said before routinely produced by passing oxygen through a solution of yosin or roge Bengal at room temperature. It is perfectly all right at 0 degree centigrade but what is the product? How do I know?

One can see that in the starting material, you have an oxygen belonging to furan and an oxygen belonging into aldehyde, when I say task specific, means that three different kinds of tasks, often the oxidizing agents do in heterocyclic chemistry. One towards the ring, other towards a particular heteroatom and third of course the functional groups or the facility of the functional groups. So, these are the three different gross classification oxidizing agents, effect of oxidizing agents, rather x n o oxidizing agents.

So, what do you think now in this case? So, that means there are three possibilities, it can attack the heteroatom, attack the facility of the heteroatom and it attacks the it can or it can oxidize the ring itself. Now, you know that two kinds of oxygens, singled oxygen, triple oxygen, grossly speaking tripled oxygens behaves like radical and singled oxygen does not behave like a radical.

Many of you know simply because in a reactions with a triple oxygen if you add innovators, radical innovators, the reaction is innovated but in case of singled oxygen it is not. Typically there are two kinds of reactions of the singled oxygen. What are the two kinds? I think I told you in last class, a singled oxygens diels-alder and in reaction, fine? Okay? To begin with also you have to remember because you will be teacher in one day or two day. How is hydrogen peroxide produced industrially two, okay?

Student: With hydrogen peroxide and reverses hike with hydrogen.

No, just you missed very important point. See conversion of oxygen to hydrogen process means it is equivalent to reduction. No, very quickly this is example of diels-aldr reactions of singlet oxygen. You are very right, I think this site order. Of course, last year also this is this, then you have to have reducing agent. Normally it is a sodium bisulfite or sodium dithionite. Sodium dithionite means N a 2 H 2 O 4 and then you pass oxygen. Actually it gets converted to treating this process, it get converted to this enthrall entra diol, right? Then it goes to corresponding diels-alder product.

So, diels-alder product means, so this is the way, actually this count. That means the basic commercial hydrogen product each produced and a time when you studied that was barium peroxide barium peroxide past but now then. Of course, then all of us know this is hemiacetal, form hemi hemiacetal forms and undergoes cleavages to give hydrogen peroxide as the final product. Then the quinol goes back, quinone and then undergoes recycling. So, this is a typical of diels-alder reactions.

So, in this case also, in this case what we can expect? We can expect a diels-alder reaction, the singlet oxygen of single oxygen. So, what next? I think this is beyond the syllabus though but I can tell you the answer. In the last class you have, now I do not know you have attend or not. There was a oxidation call crone oxidation, it oxidizing the benzalic oxygen because of the internal. There is a intra quinol itself is a nice photo sensitizer.

So, in this case also it be doing like this, what next? So, what is the next possible thing well hydrogen of peroxen hydrogen extras is a possibility. Let us say then the you get this. So, hydrogen oxidation is a possibility then one can expect that this can undergo further oxidation. Further oxidation because corresponding carboxylic acid and then you have a carboxylic acid, you have so many of heteroatoms.

So, there is a possibility that it can decompose. So, what you will have now, oxygen here, oxygen minus and then you have here double bond. That is it, what is it there is nothing but they of course during work up. So, what you will get? You will get this one and that means it starting from a heterocycle. You are getting a new heterocycle and mind it. It is equivalent to a sis aldehyde, sis aldehyde and a sis carboxylic acid and if you try to make this. Otherwise I will find it is a very tough job, first of all it is a you have to have selective oxidation done and that thing.

So, there is another way of doing it. I mean there is another way of doing it, just give you information and this is an example again a furan and you have group r. In this case the single oxygen is produced as separately t t and then light t p p is basically what it is.

No, really not, see you are talking in context of a singled oxygen. So, it has to be a photo sensitizer, a photo sensitizer. Well I will give you the product, the product is again a sis derivative sis compound, sis compound. It have this product here r and what you can see. Now, this ester is protected.

So, what you will have? I mean this peroxide also sometimes undergo to composition and this thermal conditions undergoes self decomposition to corresponding the oxocompounds. It is nothing but the ring cleave product and of course if you have a HCl and chloroform then you can go to the corresponding. The trans isomer, this at the call ester here and this carbonyl and this r.

That means you can get both the isomers and nicely with steady different way but T P P is stands for tetraphenylporphyrin. All of us know that is a classical photo sensitizer tetraphenylporphyrin. So, tetraphenylporphyrin, right? Porphyrin. Let us look at one more example of this, the on this use of singlet oxygen. This has been used and the total synthesis very complex molecule.

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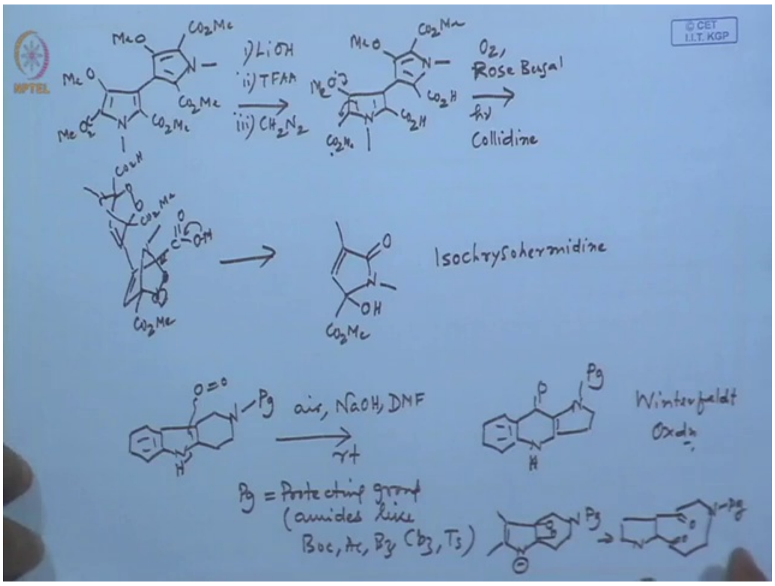

That begins with that is begins with a bipyrrolic compound. That means a pyrrole here and then one more pyrrole unit and n methyl and else I think often. I write any case, I will write here in this case I said diester 2 5 diester here of the pyrrole. Then you have also 2 5 diester on the other ring and then you have methoxy group of here and a methocy group of here, little chemistry. Then we talk about the heterocyclic part.

So, this is a very not really, it is a dipyrrolic molecule and there are molecules which are natural products and also contains the two pyrrole units. Now, we perform a sequence of reaction, first is lithium hydroxide and then triflouro acetic acid and a third one is diago methyl.

So, what you expect this is a basically a preparation of the starting material. So, first is lithium hydroxide, all of us know it is a say popular reagent for ester hydrolysis. Classically sodium hydroxide, potassium hydroxide is to be used but now in recent laboratory most people used lithium hydroxide. I think all of us know yield is very high, it is soluble and it can be controlled.

So, in this case the lithium hydroxide can be used for control hydrolysis, only for 2 ester groups control hydrolysis. For 2 ester groups there are 2, total of 4 of them, right? So, you can now since we know beat of chemistry, so you can predict, right? So, what will happen? Pyrrole units remains intact methoxy. All of us know would remain intact and this again the methoxy they intact.

Now, two of the ester groups should be hydrolyze which to ester group should be hydrolyzes. Any guess? See effect of methoxy, many of you know this methoxy. The one adjucent to the methoxy would not be hydrolyzed because of the lone pair of the oxygen. It would reduce the electrophilicity of the ester group. So, that means the other one would be hydrolyzed here.

So, in this case, that means will have 2 ester groups and the carboxylic acid, right? Then I am quite, then I have to see that well, yes trifloura acetic. That means apparently all of these ester groups have hydrolyzed but there are methods, but you can use for control hydrolysis. Lithium hydroxide is very useful, even have done it in my research career.

If you have diester with control amount of a sodium hydroxide you can do it half esters. That is a standard, then will may be will clarify after looking at the literature. Sometimes you know what happens, you know a little bit of the byproduct is formed, that is converted to the corresponding diester, that is also possible.

So, but I assume that it is mainly these two esters are preferentially hydrolyzed. Now, what next? Actually this is the most critical example of photo oxidation, again oxygen and then this catalyst that is rose Bengal. Rose Bengal, the popular catalyst and then light and something else is required because what you will see collidine, collidine and collidine is what is collidine collidine is a pyridine base.

So, you have to know now is an heterocyclic chemistry class. That means lot of heterocycles are used as a reagents in organic chemistry collidine is a methylene substituted pyridines. Then what is the product, what is the product? So, you have so many functional groups, nitrogen, etcetera. The three different kinds of modes of oxidation ring, substituent functional groups, etcetera and these I am heteroatoms.

So, in this case the answer obviously would be related to this photo oxidation of the ring and so what you will find? It will form again diels-alder thing, diels-alder intermediate with oxygen, singlet oxygen. Then you have carboxylic acid and then the ester of here and the double bond.

The similarly, the other ring also would be other ring also would be double bond and then it is oxygen, again oxygen, oxygen. Then this a methyl group and then what else? Once side you will have this carboxylic acid and other side you will have the ester groups.

So, basically you can just repeat just it down, just write only one side. That is enough, you do not have to repeat both the sides. Then what next? What next? So, up to this point this perfectly all right. So, fragmentation and what is the driving force for the fragmentation, no part of it, right? So, carboxylic acid, yes you have level oxygen etcetera but the driving force of this reaction. Actually this does not stop here, it further undergoes fragmentation reaction. So, fragmentation reaction would take place like the previous one.

So, what you will see? I think I will just only the right, this part would be the ester part. This is oxygen minus which will eventually would become O H and then what else in this case, oxygen here and this is methyl group and then you repeat the other thing. I do not, I do not want to write this. So, basically fragmentation would be taken place and this is the structure of a natural product called isochrysohermidin.

So, that means this is a very, what it means is a basically very useful synthetic transformers which can also give rise to natural products of complex nature, okay? So, this is all about this singlet oxygen but I have not got the answer yet. What are the driving force for this fragmentation, I am still looking for. I am waiting for the answer. Whenever you write reaction towards the forward directions you have to keep it in mind. Then see now you are advance level.

We have to know the reaction mechanism, reaction mechanism initial stage in b s c or first year is basically the electron book keeping when you go up little bit. Then you have to explain in terms of the transition state or grossly speaking it should speak in terms of driving forces. What are the driving forces? Why the reaction is not stopping, is further progressing towards the right direction? What is that? That is one of the I said before one more important point, why should this reaction.

So, that means weak, that means bond strength, weak bond strength of the peroxy linkage and now let us talk about one more reaction with just regular oxygen. So, I give you the reaction first, then I will tell you what it is and what is the product is a carbazole derivative is a carbazole derivative with of course this indole moiety here a ring nitrogen. So, you can say it is a actually carbonyl derivative.

So, carbazole is a two benzene ring but when you are one of the base pyridine. There is known as carbonyl derivative carbonyl derivative so is a quite famous in nucleus. Now, the simplest oxidation, often we do also in our lab for chemistry and just A r sodium hydroxide and d m f and you do not have heat anything and just room temperature and p g is transfer p g is transfer often right protecting groom protecting groom and protecting grooms are normally amides, like amides, like BOC, all of us know BOC which are oxy carbonyl acetate benzoid and C B Z.

I think carboxy benzyloxycarbonyl C B Z and tosyl all of them actually belong to the amide groups and this is, and most of the cases nitrogen protecting groups are amide protected groups, okay?

So, what do you expect out of this reaction is a very simple reaction. Though no complication, just oxygen, plane oxygen and there is no photo sensitizer. So, say base catalyze reaction, base catalyze reaction and apparently it proceeds through with the tripled oxygen oxidation and the product I will give you, the product is now is a reagent product.

That is it, what is it is a quinoline derivative is a not really quinoline derivative is little something different but any case what you see here? The middle ring got expanded and the right terminal ring got contracted. So, if you overall look at it is an oxidation reaction because oxygen incorporated. So, this is this side of reaction is a pretty well known in heterocyclic chemistry and this is known as winterfeld oxidation.

So, what is the prerequirement? The prerequirement is a essentially the N H, if you have N H. N H would form a negative charge here and then eventually after delocalization etcetera it will captured an oxygen up here and it is a four member ring. That means it is a formally kind of a 2 plus 2 kind of reactions. 2 plus 2 is formally but it goes by the anion formation, nitrogen anoin formations. This anoin forms this, this oxygen attacks here. This anion goes to these and this oxygen minus is come back and then you can write an intermediate of this kind dioxy. So, dioxygen you can say, okay?

Then what? Then all of us know when the 2 plus 2 cycloadditon takes place. The next normal reaction is again 2 plus 2, the 2 plus again in this case the driving force is the weak peroxyl linkage. So, it would form, it would form I mean this then oxygen up here that is it. So, what next? You can guess now.

Just intramolecular l, all type of reactions l, all type of reactions. So, since we know the product when it forms a carbonium up here, it would undergo arlol type of product with this. So, this is also quite prevalent in heterocyclic chemistry. This internal oxidation, that means in summary oxygen is a very good useful oxidizing agent.

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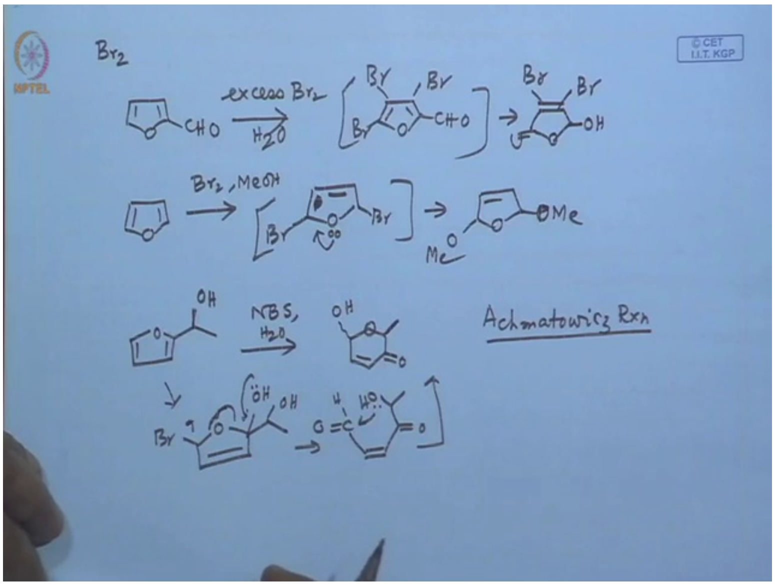

Let me go to the another kind of reagent which is a basically reagent. I think all of us know the bromine, bromine in heterocyclic chemistry, also is pretty good oxidizing agent. For example, if you start with a furan compound and you use excess bromine, excess bromine so what do you expect? Excess bromine acid, yes I would assume acid probably and what else? I will give you a hint. I will give you a hint and let us say this is taught in b s c. If you take furan and add bromine and in adjust it one equivalent of bromine and methanol, what you will find?

Right, because the intermediate, sorry the intermediate diagram compounds are pretty reactive by virtue of the having lone pair on oxygen and all of us know oxonium ion is more stable because of the lone pair effect. So, that means this like mom chloride, mom chloride all of us know mom chloride. They are pretty reactive because of the oxygen lone pair, it produces stabilizes the adjacent carbocation.

So, on the similar ground this sort of intermediate would pretty reactive and so the product would be all of us know the bromine would be substituted by methoxy on the both the sides and you get this product. So, can say one can view this reaction as an oxidation reaction. If you look at the number of oxidation level or the, or else you can say dearomatization process, so oxidating dearomatizations, okay?

In this case also you would expect a very similar reaction, but since equivalent of bromine is quite high so one would assume this nuclear bromination. Also nuclear bromination would takes place. That means what I can say C H O here and this let us say the nuclear bromination also can takes place, right? Nuclear bromination can take place and when I say bromine 5 member ring bromine means.

Of course, the water is there and this bromine anything else you can expect. Eventually you just sit down and do this work and you will find, it will give a nice compound. Again a sis derivative, sis derivative will hydrolyze and then ring close and eventually you get this sort of aldehydic carboxylic acid aldehydic carboxylic acid.

Now, if you just change the substrate, say initially it was furan. The next example was furan carboxyldehyde. Now, we have a substrate, let us say just little change. So, now hydroxy furan hydroxy furan and then the reagent also is change little bit NBS and water NBS and water it what is it equivalent to bromo bromohydrin, bromohydrin bromonium ion and OH. We do a this is a nice again a sort of an bromine addition kind of things ring opening and ring closing.

This reaction has been termed as now achmatowicz reactions. Achmatowicz reaction is under the name of a Polish scientist. Achmatowicz reactions, what is it is a very useful reaction though again an oxidative dearomatization kind of reactions. The product that is formed these double bond and then you have this hemiacetal kind, means oxygen here. This methyl group how do you view it mechanistically? Mechanistically one can see this.

Since it is a bromohydrin you can write that this brumation takes place. This hydration takes place, whichever you like, then you have OH group of here and then just it opens up and so what will see, this is double bound here and then this would be equivalent to aldehyde, right? This is equivalent to aldehyde and then this would be equivalent to a ketone and now you have this OH and this is the methyl group. This is the methyl group, right? What next? I think all of us know the ring closing, ring closing, the ring closing takes place.

This a very useful reactions and this particular reaction why it is now named as achmatowicz reactions. I mean if you look at the mechanism is a very simple one, addition ring, opening ring, closing chemistry wise is not a great one but it has been used on several occasions. Several occasions especially this substrate, the pyranone is very useful in many synthetic transformations. Let me give you a quick example like many, you will be able to tell me the answer. I think I will keeps some of the examples.

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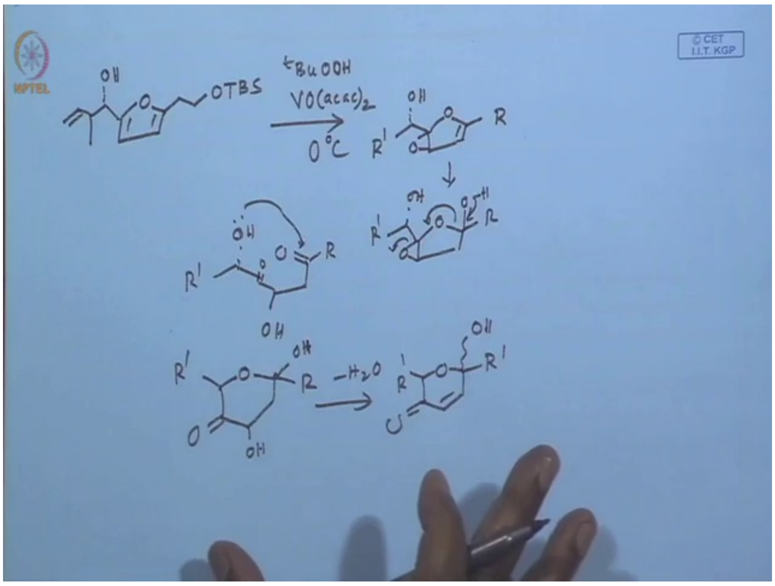

Let us look at one more, a very similar kind of oxidative dearomatization. Here is a furan, then you have a side chain with TBs tertiary, butyl skyline and the other side what will have? You have again a side chain, mind it you have a now O H group of here. So, it is not a furan furan carboxylate, it is a furan furan alcohol. Then the reagent here you see here the reagent again, we are talking about this proxy compounds.

Now, it is a separate one, now so initially we talked about singled oxygen, tripled oxygen then brominating agent, bromine and NBS. Now, we are moving towards the proxy reagents, so tertiary butyl hydroperoxide is basically a proxy reagent based on hydrogen peroxide but solvable in organic solvents.

Now, what happens if you react these with and then vanadium oxo acetylacetonate. That is catalyst and the 0 degree centigrade does it demand, do anything about the reaction. This combination of reagent I thought you memorize whole book of Kelothars, anybody has memorize kelothars book?

Student: Epoxidation.

Epoxidation reaction, surface epoxidation reaction, surface epoxidation reaction. So, what do you except out of it? But in these case is a furan case epoxidation. If you recall it requires the presence of a hydroxy group. Epoxidation is requires the presence of a hydroxy group, with that hydroxy actually coordinate the titanium, in these case is a vanadium. So, that and this is not an asymmetric portion, it is a know chiral version.

Now, what is the product? I think you would be able, you should be able to write the product, right? Again what I said is a dearomatization program and let us should we work it out may be. So, what you do? Begin with this, I think we will just write R on this side and R on this side will take this OH group because I would be participating the reactions, let us R prime, what next epoxidation.

Let us say we do this epoxidation, that is it the two double bounds i-i have done epoxidation on the side of the hydroxyl. When nobody know the what happens but it is likely reaction would be directed by the hydroxy towards this double bound favoring to it and then you have a double bound here. What next? Next may be seen to hydrolysis. Let us say just simply hydrolysis, that means water addition take place.

This is OH and this is r prime and this is R and this has simply water addition base and in the during the reaction and so it again, it opens up and this. So, what will see then will have the ketone on this side, R side this then will have a hydroxyl. Then one more ketone, then you have one more hydroxy and then R prime, right? So, what we except then next? Next would be ketalization.

So, that means will have, now that means1, 2, 3, 4, 5, 6. So, we can blindly write, you say pyridine ring structure, right pyridine ring structures. You have OH of here this, then R and on this side will have R prime. Then next this one is this and this OH of here right and this OH this at some point it loses water, it loses water.

So, what you get? What you get is a pyronon. So, you get a pyronon and this is OH and this is R and this is of course then R prime. So, at net result what is the net result is very similar to these you say is a new version of basically aconitase reaction. Only thing that the reagent is different, reagent is different. It is the sucrose reagent and this, so this a nice. That means and in this case it is a peroxy compound, oxidizing agent is a peroxy, not the NPS, okay? Now, look at one more, the important reaction this is selectivity.

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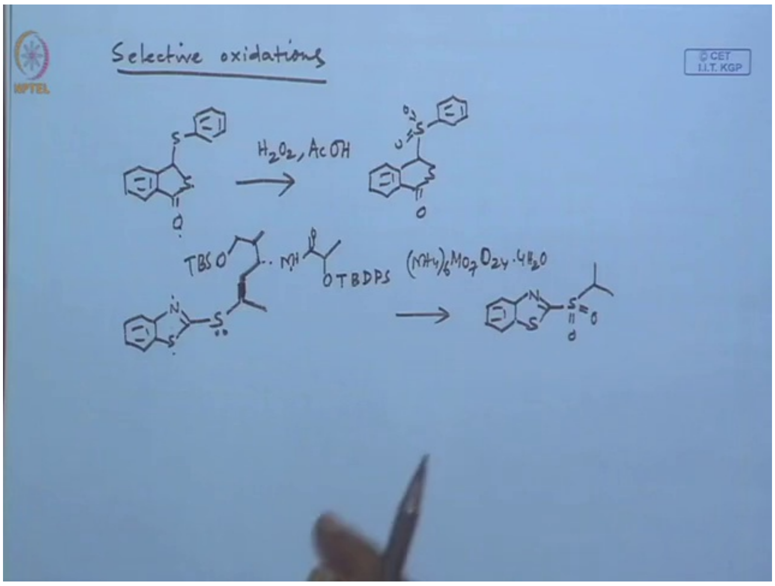

That means selective oxidations when I said to begin with task specific many the reagents are sometimes very specific, very specific and in this case very selective. Let us say I give you an example from my lab, where will have we made few years ago a compound of this kind.

So, obviously it belongs to a heterocyclic compound. Now, I treat this with a peroxy compound, hydrogen peroxide and acetic acid. I think all of us know what it is. It is a equivalent to peracetic acid, now you have all kinds of possible oxidations is an oxidizing agent all of us know. Then we have a thioester, we have a sulfur, again you have a neighboring alpha hydrogen, you have another sulfur.

So, which one do you expect? Selective oxidation would be taking place and you search one single oxidation, replace either at the ring or at the alpha position or at the heteroatom’s and then you have two heteroatom’s, then one of the heteroatom’s. The guideline is very simple, the one that is most electron deficient would not be reactive.

So, that means actually in these sulfur is very many of you have to remember. At the end of the course you have to remember of all heteroatom sulfur is most susceptible to undergo oxidations. Even nitrogen of course, provided all other things are its very similar structurally. All other things are similar, sulfur is most want to undergo oxidation followed by nitrogen. Of course, oxygen itself is oxygen. So, there is no question, that means when you talk.

Now, when you comes to the differentiation between the two different kinds of sulfur, the sulfur which is of course more nucleophilic in nature and in these case because of the adjacent carbonyl the ring sulfur is not really very nucleophilic. So, the oxidation takes place, the oxidation takes place at the other sulfur and the yield is very good.

So, pretty wanted a sulphone that is what we got. That is what we got and let me give you one more examples. One more example this is little complicated but you do not have to write, memorize. Though just get the point here, this is benzothiazole, benzothiazole then you have a sulfur up here and then is a may be wrong somewhere. May be I have no idea, double bond, sorry.

This is not a double bond, this is not double bond, sorry single bond. This methyl group here, then you have I mean all kinds of groups here and there this is this is TBS and then you have a amide point here, then you have again a in these case TBDPS, okay?

So, by giving you all these now does it tell you anything about this structure? Anybody can recall what is the structure famous for.

Student: Close.

Close is close, this is x is close actually. This is a reaction, this is reactions you have been thought in the last year, this is A. So, what you do, you selectively oxidize and make a sulphone up here and the rest is same is a Julia Kocienski reactions. Julia Kocienski reaction means you said little different.

So, what you do, you require that means you require a very selective oxidation, very selective oxidation and what is the reagent? Ammonium molybdic acid and this is quite often used in one of the lab in IIT, which one is it comics lab and they often use the Julia Kocienski reaction but for us you have to what you have to learn is a very selective. What you see here? You have all kinds of sulfur nitrogen ring, all these things.

The thiazole ring, it is not destroyed, you have to different kinds, you have 3, 2 different kinds of nitrogen. There is a thiazole nitrogen and is amide nitrogen, amide nitrogen as you obvious. The lone pair is delocalized towards oxygen, that is not available but in these case you have a nitrogen free lone pair of free at the nitrogen of benzothiazole. That is not getting oxidized, you have two different kinds of sulfur. All of us know this sulfur of the ring is involve to the aromaticity of the system.

So, what is available then you have a three sulfur, you can selectively oxidized to the corresponding sulphone. Next item of course, this is a very useful one, many of you probably do not know this is magnet dioxide. How is it made? Magnet dioxide, how is it made? Magnet dioxide is made from manganese sulphate and potassium permanganate. It can be used in three different conditions, neutral basic acidic but most of you know in organic chemistry we use the neutral version occasionally, use acidic version and the basic version is normally is not used, it is not very strong powerful oxidizing agent.

So, the most powerful oxidizing is magnet acid. In acidic medium followed by the neutral one but in heterocyclic chemistry what you will see? It does not touch the heteroatom’s unlike the hydrogen processor at the peroxy compounds, where you can found the anoxide sulphone, etcetera. The example you will see here.

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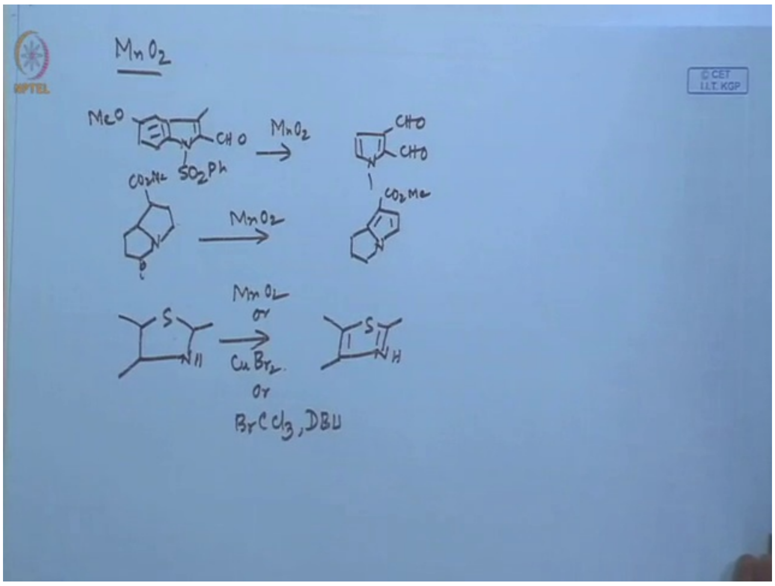

It is an indole derivative where nitrogen is protected as the sulphone and then you have an aldehyde up here. If you try to do this oxidation with magnet dioxide what you will see it only specifically gives you this side chain oxidation, rest remaining same only, side chain is getting oxidized, okay?

So, which is equivalent to some sort of you can say this selenium dioxide oxidations. Many a times selenium dioxide also carry the same thing. That means this nitrogen is getting remaining unexpected and the ring of the indole ring is not getting affected. Let us take about, let us this one more pyrazolidine ring system and you have a let us say carboxylic ester group up here.

Now, if you try to do this is a important though magnetic oxide. So, these are the example. Basically from there you can just draw this or rather you can estimate the sense of oxidizing power of different oxidizing agents and in the first case there are what is that.

Student: Carboxylic acid.

Tell me again.

Student: The ring that does not contain that carboxylic.

It could be oxidized P H or let us say that is what I would assume first. Actually the alpha position or automation nitrogen would be oxidized. The corresponding ketone, that is what I would expect because nitrogen you can assist the formation of the carbocation alpha to it.

So, one would expect a double bond up here, oxygen and or on this side but this is very good in heterocyclic case especially for dehydrogenation is an replacement of D D Q and one of the rings would be dehydrogenated. In these case which one, guess there are two rings, one without carboxylic acid, one ester, one is free. Actually the one with carboxylic acid because all of us know the most substituted double bonds are more stable.

So, this is that classically you can do it and one more example probably for this aromatization like thiazole. These thiazoles are very useful again and heterocyclic chemistry and often these are made and how do you aromatize D D Q as expensive toxic. All these things but one can just nicely do it with magnetic oxide, magnetic oxide alternatively or often this cupric bromide is used or this is something probably you do not know.

These tri, sorry bromo trichloromethane and D B U, bromotrichloromethane is a nice actually brominating agent. It brominates alpha positions, then dehydrohalogenation take place and eventually you gets the aromatizations done and then I have one more example. I think I will skip but quite interesting example, I think I will give you.

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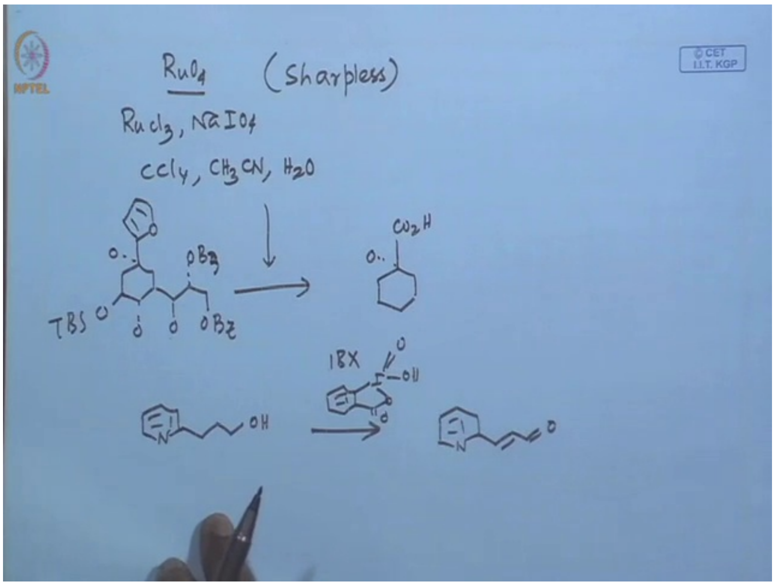

I think many of you know I guess. Ruthenium tetroxide, ruthenium tetroxide is a very useful one, very useful reagent. I mean often you do not use it but it is and one of the conditions is ruthenium trichloride. Then sodium periodate and then triphasic system. Triphasic system means C C l 4, then acetonitrile and water. This was published when we did, okay?

So, this is due to again sharpless fluid is like he is only did oxidation and this is a very good method. A very good reagent at ruthenium trichloride sodium periodate is equivalent to ruthenium tetroxide. It can do many oxidations but just I will in the context of heterocyclic chemistry I will just tell you only one example, that is a fural substituted compound.

Then you have so many oxygen here and there all these things, then you have a side chain. This oxygen stereochemistry everything I mean here and there different oxygen's, I will not write the full structure. When you apply this reagent what did you expect these are all this actually benzyl group. That means benzoid, sorry benzoine.

So, benzoin groups all these one oxygen, one of these oxygen is actually TBS. So, I mean it does not matter, that means all these oxygen's are protected now. So, what do you expect again? I though this reagent in the last year it is a one of the very useful and very unique oxidizing agent, many times it does a lot of important thing, any idea, any answer from the class, no, okay?

So, that means furan here search as the a carboxylic acids. If you recall, you have a different oxidizing side chains on the benzene and if the benzene is electron rich that can be oxidize to the corresponding carboxylic acid and side chains remaining other. That means this reverse of potassium permanganate, if you take toluene it will oxidize to corresponding benzoic acid but if you want.

Let us say from toluene to convert acetic acid, how do you do ruthenium. Ruthenium tetroxide and what else let me just these are all miscellaneous. Let us say kind of reaction, for example you have now in heterocycle, you have a side chain oxidizing agent and then I B X.

Anybody know what is the structure and some of you know I guess is a benzene ring is iodine and then is a carbonyl oxygen and then what you will have double bond up here and O H isobenzo oxazole. I stands for iso, B stands for benzo and X stands for oxazole. IBX is a now common is an household name in organic chemistry who uses exclusively in our department. Again soumic routinely uses IBX I think.

Once upon a time he is to make it in grams and grams what do you expects in hetero compound is in heteroatom. So, it does not undergo in oxidations, it does not undergo oxidizing dearomatization. What it does? It gives a interesting thing here, oxygen this and then this one. That means it is oxidizing the alcohol and also it induces the deoxygenation, okay? We have very few minute, I think I will go to the next. I mean I have skip, I am skipping this devis oxidation I think.

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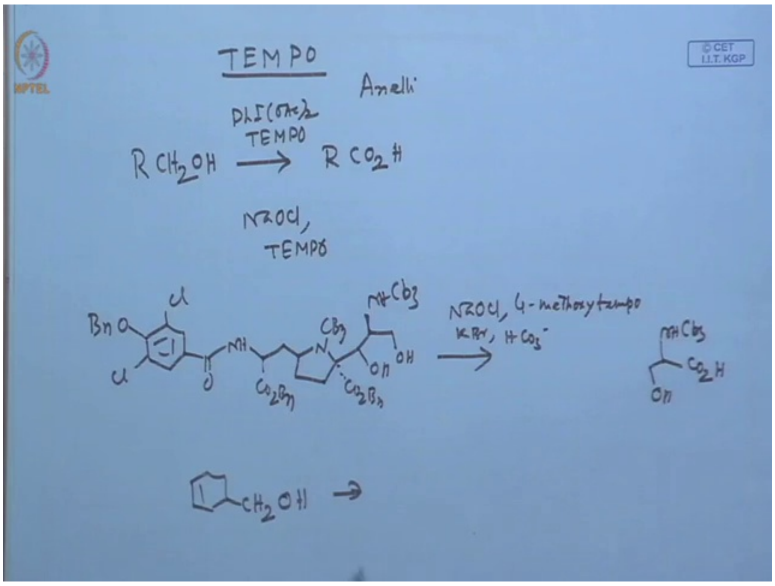

I will have one more important oxidation, this is I think this is the Yings of heterocycle in oxidation is not the oxidation of the heterocyclic system. It is the heterocyclic based oxidizing agent that is used in literature. For example, if you are to require, if you are if you require to oxidize a primary alcohol to the corresponding carboxylic acid so how do you do it?

Sodium chloride and tempo, fine? I think you are very right. Actually the name of the reaction I write, if you do not want to remember nice perfect, all right? Anelli oxidation it was a discovered in 1987 and this is yes, you are I mean there are different kinds of the combinations. One can do phenyl iodonium acetate and tempo, this is one. This is one conditions.

The other could be sodium hypochlorite, that means bleaching powder and tempo. So, I think the original one with bleaching powder, recent version is sodium, sorry potassium phenyliodonium diacetate. What is the beauty? I think I will just give you only one example, that will tell you what is the beauty of this reagent.

The structure of the molecule is like this, you have a benzene ring like chloro and dichloro. You have a benzyl and then you have amide here, then you have a pyrrolidine structure. Then you have is a diol one-three diol and then you have nitrogen up here, nitrogen. Then C B Z protecting group and here you have a carboxylic protecting group.

So, likewise I mean you have so many functionalities, right? So, many functionalities basically now if you this anelli oxidation, in these case is a 4 methoxy sodium recopies like this sodium hypochlorite. Then 4 methoxy tempo that was the original one, actually 4 methoxy tempo then potassium bromide catalytic and bicarbonate sodium bicarbonate. What you will see, it does not oxidize the benzylic C H 2.

It does not oxidize the benzene ring, it does not oxidize the nitrogen, it does not oxidize this nitrogen. This nitrogen is protected as C B Z and you have a secondary O H group. It is not oxidized, only the last one is oxidize. That means this is and then C B Z and this one gets converted to the carboxylic acid and the oxidation of carboxylic acid is not that easy though. For example, if you have ethanol you want to oxidize to carboxylic. What is the method, not many methods, I mean classically we is to do all these oxidizing agent potassium permanganate potassium all these things, okay?

So, but if you have little complex system for example at one point we try to oxidize these two corresponding carboxylic acid, how do you do it in our lab? We do right, how do you do it? You can a day is to stuff reason being you have a double bond present now.

So, that restricts your choice but if you have this kind of reagent some which are very selective towards the oxidation of the alcohol to this that to we see here primary one. There are many methods in the presence of primary, you can oxidize the secondary, right? There are many methods, all the hypochlorite based oxidizing agents are actually selective towards the secondary alcohols, not the primary one but what you see here in this?

It is the primary one, that is takes care of I think I have skipped actually quite a few but may be if the time permits towards the end of the series semester we will talk about it. Next time we will talk about what are you suggest something, you want to know you are eager to learn, obvious.

Student: Nucleobases.

Nucleobases, so rather not chemistry, there in nucleobases. Yes, that is one in only nucleophilicity, etcetera, etcetera.