Reagents in Organic Synthesis
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Oxidation mediated by DDQ, CAN and SeO_2
Keywords: DDQ, CAN and SeO_2

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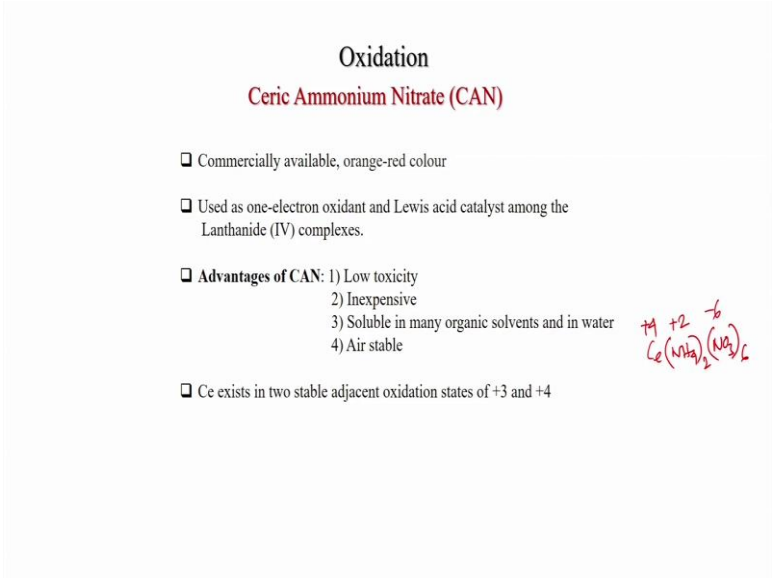

Welcome again to the MOOC program. Today we will discuss three oxidizing agents. First one is ceric ammonium nitrate which is called CAN, then DDQ and last is selenium dioxide SeO_2. So ceric ammonium nitrate is commercially available and this is orange red color, used as one-electron oxidant and also Lewis acid catalyst among the lanthanide complexes. Advantage of ceric ammonium nitrate is it's low toxicity, it is inexpensive, it is soluble in many organic solvents and also in water.

It is also air stable. And cerium exists in two stable adjacent oxidation state, plus 3 and plus 4. So if you see the structure of ceric ammonium nitrate, so 6 nitrate is bringing minus 6 and 2 ammonia is bringing plus 2 so cerium is here, plus 4. So what happens it on reduction it can go to plus 3, another oxidation state after oxidizing. Electronic configuration of cerium in ground state is xenon 4f 1 5d 1 6s 2.

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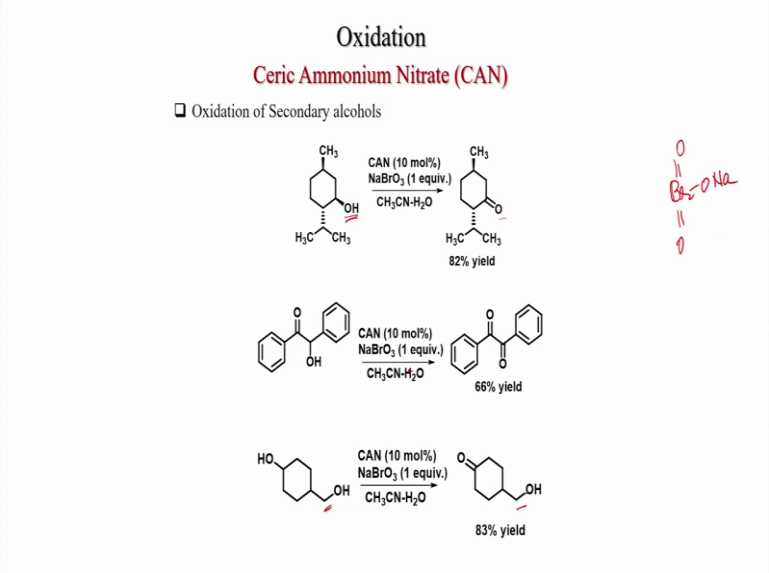

So ceric ammonium nitrate has been used in many oxidation reaction. Mainly first we will discuss oxidation of secondary alcohols. So here you can see the secondary alcohol is selectively oxidized to the carbonyl compound with catalytic amount of ceric ammonium nitrate and another stoichiometric oxidant sodium bromate. So if you see the bromate structure, so this is sodium bromate. This is used as stoichiometric oxidant with catalytic amount of CAN and these two chiral centers are undisturbed in this oxidation reaction.

Similarly this hydroxy ketone was oxidized to benzil with ceric ammonium nitrate and sodium bromate 1 equivalent in acetonitrile water solvent. And this is very interesting reaction. Here one secondary alcohol and one primary alcohol is there and under this condition ceric ammonium nitrate 10 mole percent, sodium bromate 1 equivalent in acetonitrile water, only secondary alcohol is getting oxidized. So when there is a primary alcohol then simple primary alcohol may not be oxidized with CAN.

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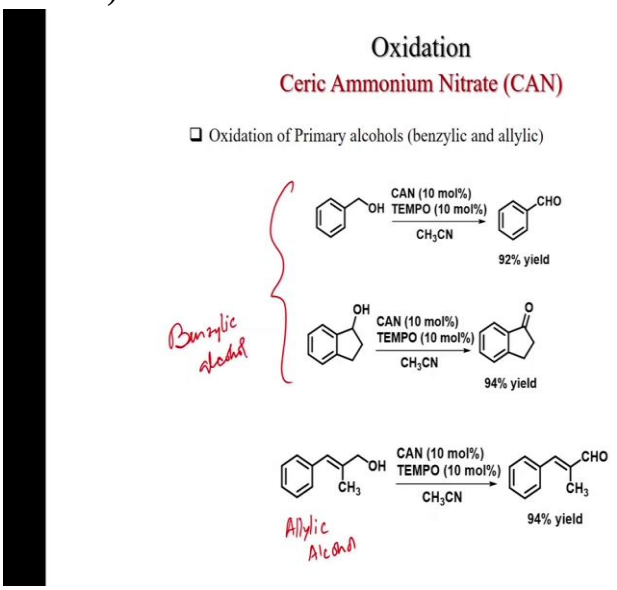

And we will see now which kind of primary alcohols can be oxidized with CAN. So primary benzylic and allylic alcohols which are more reactive, that can be oxidized in ceric ammonium nitrate. And here one example is benzyl alcohol with ceric ammonium nitrate 10 mole percent and 10 mole percent with acetonitrile solvent it gives 92 percent yield of benzaldehyde.

Again this alcohol, this is dihydroindanol, this under oxidation with CAN and TEMPO 10 mole percent each in acetonitrile gives this ketone 94 percent yield. And this is an example of allylic alcohol. And these two, whatever we discussed, these are benzylic alcohol. So allylic alcohol also can be oxidized with ceric ammonium nitrate and TEMPO each 10 mole percent in acetonitrile solvent it gives 94 percent yield of the product.

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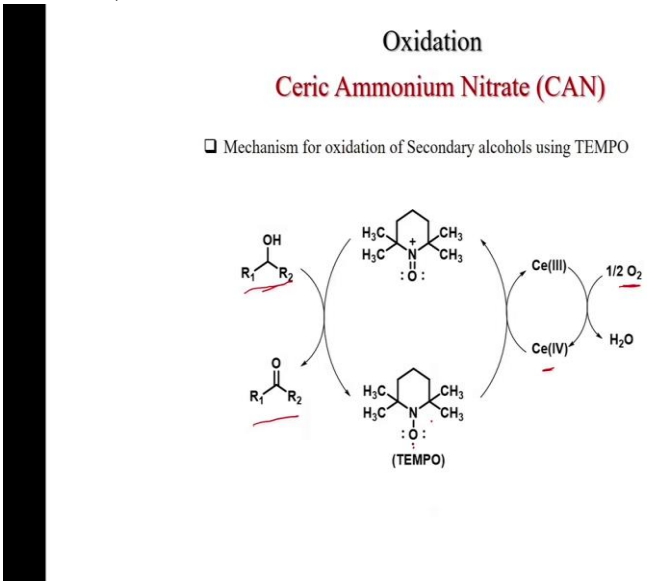

And now we will discuss the mechanism of oxidation of secondary alcohols using TEMPO and ceric ammonium nitrate. So this is the TEMPO, this tetramethylpiperidine N-oxide, there is a radical, this one and this is also single electron oxidant and ceric 4 to ceric 3 this is also single electron oxidant.

So what happens TEMPO first goes to the N oxide. It gets one electron oxidization by cerium and cerium 4 becomes cerium 3 and this species, this actually oxidizes the secondary alcohol to the ketone. And when cerium 4 becomes cerium 3, it again reoxidizes to cerium 4 by oxygen. So this reaction you have to do under oxygen atmosphere and then oxygen will get reduced to the water.

So this is the whole catalytic system, this is bi-catalytic system that TEMPO also is getting cyclized in this reaction and cerium 4 also getting cyclized in this reaction. So TEMPO is getting oxidized by cerium and cerium 3 is getting oxidized by oxygen.

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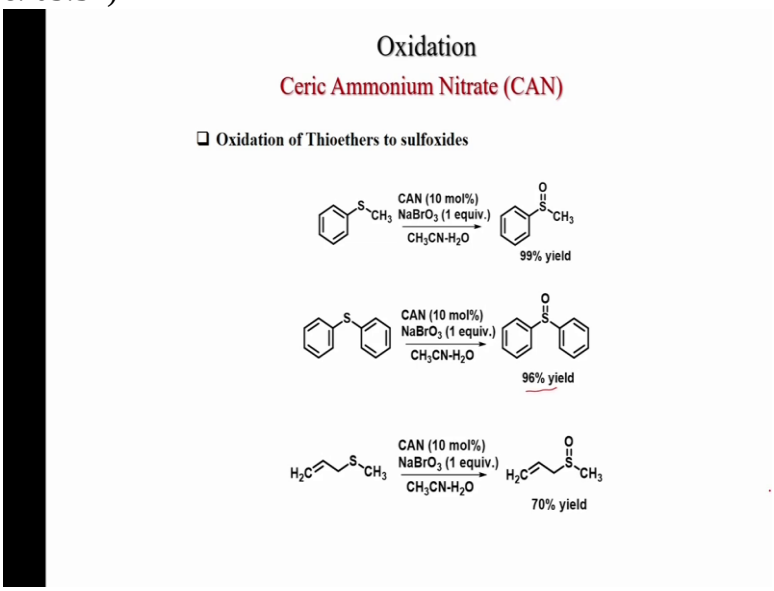

Another important reaction that ceric ammonium nitrate performs is oxidation of thioethers to sulfoxides and this thioether with ceric ammonium nitrate and here again you have to use sodium bromate 1 equivalent you get the sulfoxide in 99 percent yield. Both aromatic system and thioether this also can be oxidized with ceric ammonium nitrate, sodium bromate 1 equivalent acetonitrile water, it gives 96 percent of this sulfoxide.

Also both alkyl group is there. This also oxidized, one allyl and methyl group is there under ceric ammonium nitrate 10 mole percent, sodium bromate 1 equivalent and acetonitrile water it gives 70 percent yield of the sulfoxide product.

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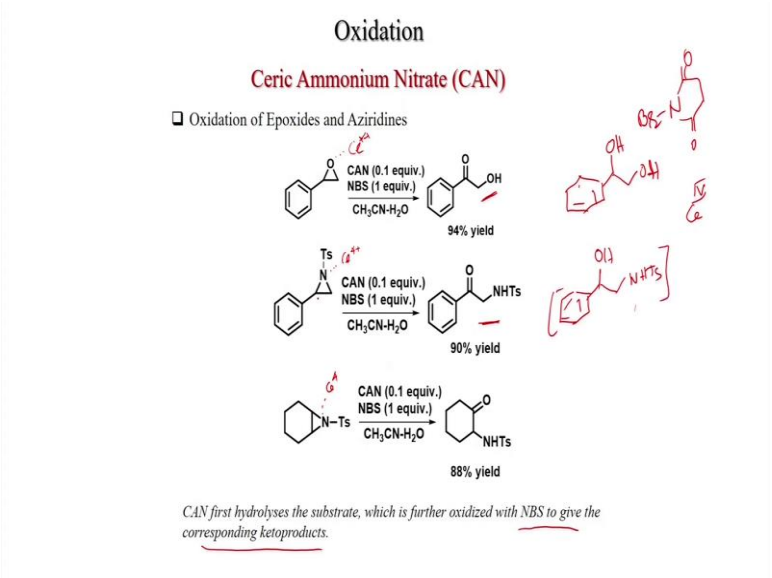

Oxidation of epoxides and aziridines, ceric ammonium nitrate also perform this reaction. Here you can see this epoxide is there, styrene epoxide and it in 0.1 equivalent of ceric ammonium nitrate and 1 equivalent of n bromosuccinimide. So this is N-bromosuccinimide, 1 equivalent in acetonitrile water, it gives this 2 hydroxy acetophenone. The alcohol is on the primary and the carbonyl is the secondary, this is the ketone.

And here also this aziridine, n-tosyl aziridine, can be reopened and followed by oxidation with ceric ammonium nitrate, NBS in acetonitrile water it gives this amino ketone in 90 percent yield. Also cyclohexyl containing aziridine can be also opened under this condition and gives this amino ketone with cyclohexyl group in 88 percent yield. So what is the mechanism of this reaction?

And this most likely mechanism that CAN first hydrolyse the substrate. So when water is there and ceric ammonium nitrate also is Lewis acid, cerium 4, so it will bind to the, it will coordinate with the epoxide here, aziridine also will coordinate with the cerium plus 4 and then water will attack and will give the alcohol and that alcohol will get oxidized with NBS to give the corresponding keto products.

So this intermediate, this reaction intermediate can be considered a diol. And we have already seen that this diol, secondary alcohol will be selectively oxidized with this ceric ammonium nitrate. Here also this, here may be this product; this intermediate will be first formed. Water attacks from this center here and you get this intermediate and then after oxidation with N bromosuccinimide you get this amino ketone.

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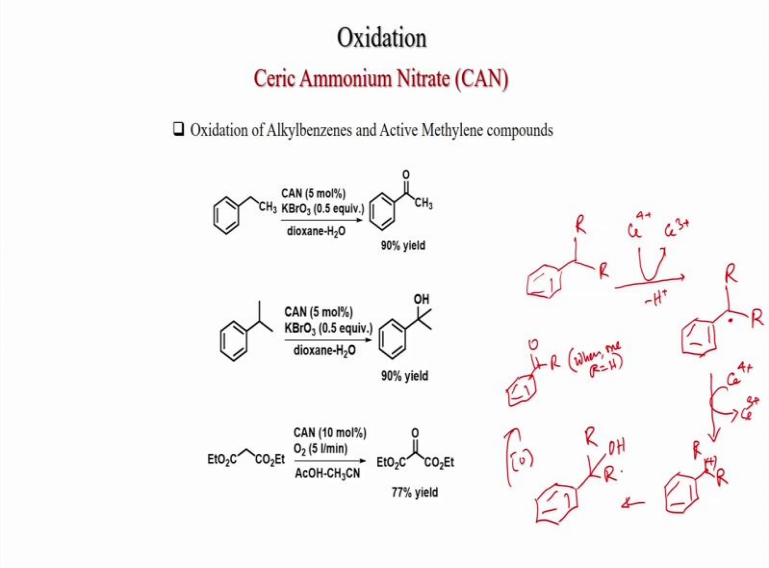

Oxidation of alkylbenzenes and active methylene compounds, under certain conditions this ceric ammonium nitrate also oxidize alkyl benzenes like here ethyl benzene is there. Ceric ammonium nitrate 5 mole percent, potassium bromate 0.5 equivalent and dioxane water you get acetophenone 90 percent yield.

Also, when 2 methyl group is there, isopropyl benzene can also, under this condition because there are two methyl groups is there and selectively only the tertiary alcohol is formed in 90 percent yield under this condition, ceric ammonium nitrate 5 mole percent, potassium bromate 0.5 equivalent in dioxane water.

And diethyl malonate, here also this proton is quite acidic and under this condition it has been found ceric ammonium nitrate 10 mole percent oxygen 5 liter per minute, acetic acid-acetonitrile solvent, it can give this keto-ester product. So what will be the mechanism of this reaction? So we can think that first a single electron oxidation will happen so you get first a radical and again, this is single electron oxidant again it becomes formation of a carbocation.

And this carbocation under this condition will give alcohol and when one of the R is hydrogen then it will be benzyl alcohol and benzyl alcohol we know that under ceric ammonium condition you get the ketone. So it can further oxidize to this, and one R is equal to hydrogen. So if this is the secondary alcohol then you get the ketone.

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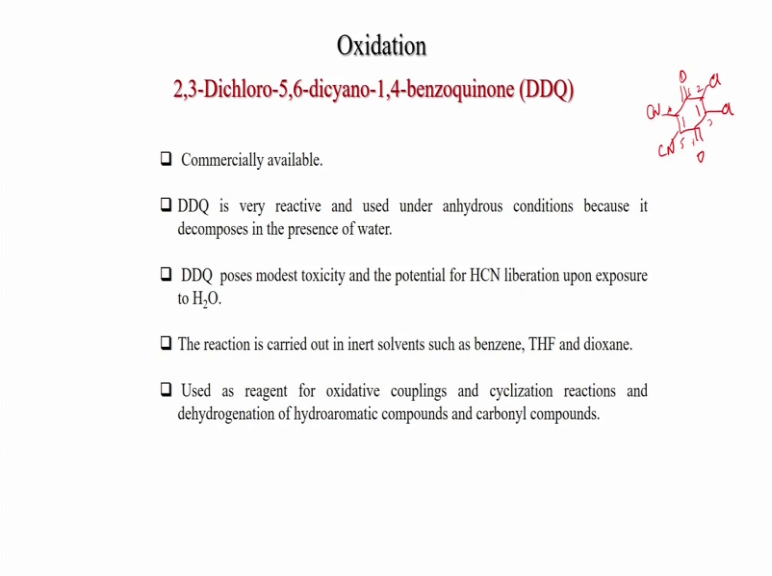

Now we will discuss DDQ, this is, full name is 2, 3 dichloro 5, 6 dicyano 1, 4 benzoquinone. So one side 2 chlorine group is there and another side two nitrile or cyano group is present. So it is called 2,3,1,2.3, 4, 5, 6. 2.3 dicholoro, 5, 6 dicyano, 1,4 parabenzoquinone. This is also commercially available. DDQ is very reactive and used under anhydrous condition.

So unlike ceric ammonium nitrate, ceric ammonium nitrate is water soluble and you can do even reaction in water, acentonitrile water we have seen but in DDQ you have to use under anhydrous condition because it decomposes in the presence of water. DDQ poses modest toxicity and the potential for HCN liberation upon exposure to H_2O. So it, may be modest toxicity because it can liberate HCN. The reaction is carried out in inert solvent such as benzene, tetrahydrofuran and dioxane.

Used as reagent for oxidative couplings and cyclization reaction and dehydrogenation of hydroaromatic compounds and carbonyl compounds. So hydroaromatic compounds to aromatic compounds and carbonyl to alpha, beta unsaturated carbonyl that we will see in details.

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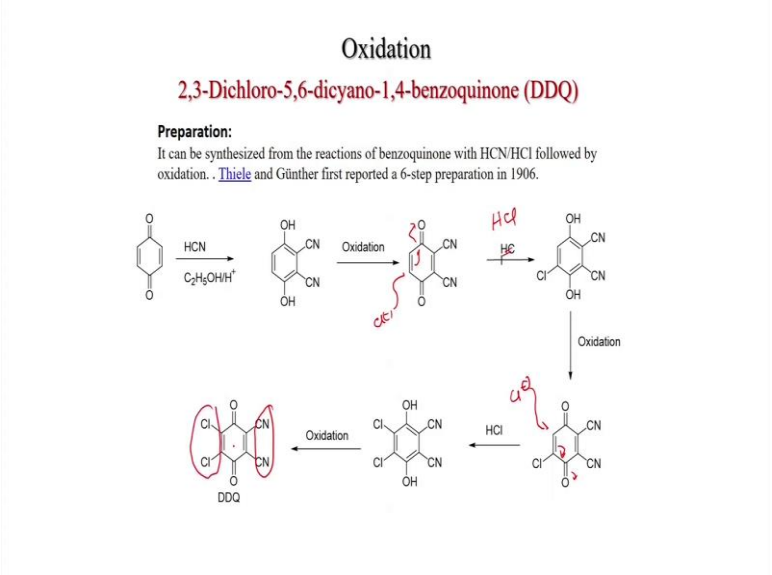

So this compound was first reported in 1906, Thiele and Gunther first reported a 6-step preparation. It can be synthesized from the reaction of benzoquinone with HCN / HCl followed by oxidation. So this is the first step, that HCN adds in ethanol H plus condition, you get two cyanide group from the same side and you get this hydroquinone.

Then after oxidation it becomes quinone again and this is HCl actually, so HCl adds here Cl minus, if Cl minus adds here and then after aromatization you get this hydroquinone and again oxidation to quinone and then again another Cl will come, HCl so again it will react like this and then after aromatization you will get this hydroquinone and oxidation again you get the quinone. So this is DDQ, so two cyanide group is one side and two chloro is one side and keto groups are in the para position each other so 1,4 para benzoquinone.

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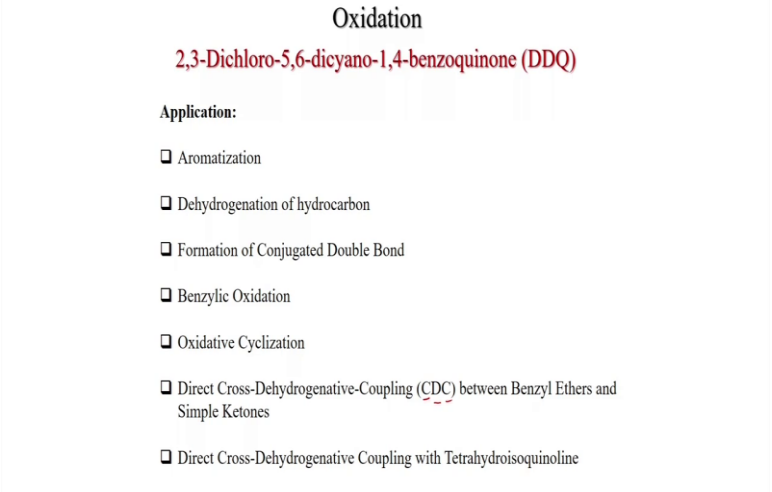

Its application, it is applied in many reactions. One of them is aromatization. If you have dearomatic compound then you can put DDQ, it will aromatize. Dehydrogenation of hydrocarbon, sometimes hydrocarbon has been dehydrogenated to get a double bond.

Formation of conjugated double bond, that we will see, alpha beta unsaturated carbonyl compound you can generate, also a double bond conjugated with aromatic system we can generate, benzylic oxidation you can, we will discuss the benzylic C H can be oxidized to ketone, oxidative cyclization reaction also is well-known.

And direct cross dehydrogenative coupling that is CDC, cross dehydrogenative coupling between benzyl ethers and simple ketones, also other nucleophiles. And direct cross dehydrogenative coupling with tetra hydroisoquinoline. So these reactions we will discuss.

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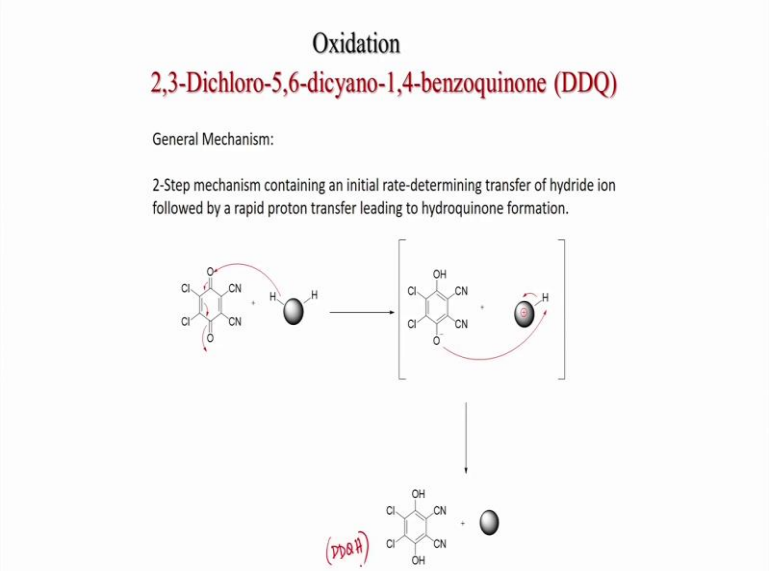

What is the general mechanism? How DDQ operates in the reaction? So this is generally two step mechanism containing an initial rate determining transfer of hydride ion followed by a rapid proton transfer leading to hydroquinone formation. So this is the main reaction that happens actually, that H minus first react, also electron also can react first here, because this is a electrophilic compound, this parabenzoquinone so it is electrophilic compound and then H minus first react here, you get this system, O minus is there.

This hydroquinone there is O minus and now this O minus is reacting to the H plus and then you get this motif. And ultimately one H plus and H minus, first H minus and then H plus

react with the DDQ to get this hydroquinone, or DDQH, this we call sometimes DDQH, hydrogenated DDQ.

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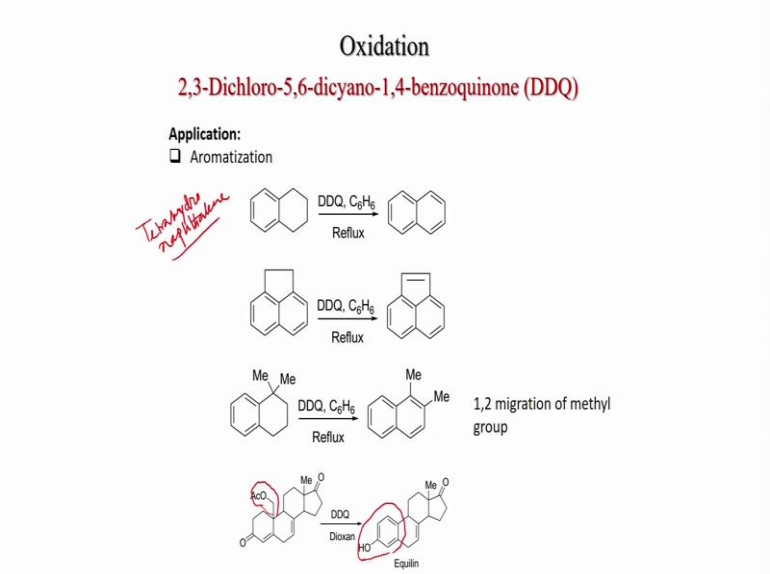

First we will discuss aromatization reaction and this H, tetrahydro naphthalene, tetrahydro naphthalene, if you put DDQ, we generate two double bonds and it gets aromatized under benzene reflux condition. Also if you have this system this will also aromatize. There will be generating a double bond and then this compound you can generate under similar condition, benzene reflux.

Here if you put two methylated i.e 1, 1 dimethylated tetra hydronaphthalene under DDQ benzene reflux condition, you get this 1, 2 dimethyl. So 1, 2 migration of methyl group is observed along with the aromatization. The mechanism we will discuss and here if alpha beta unsaturated ketone is there, then also aromatization, this group liberates because the aromatization is a very facile process.

So this group liberates under DDQ dioxane condition and you get this phenol motif. So this is very interesting. So one double bond will happen here, double bond and then it will be pushing so that this will leave and you will get the aromatization. This we call equivalent.

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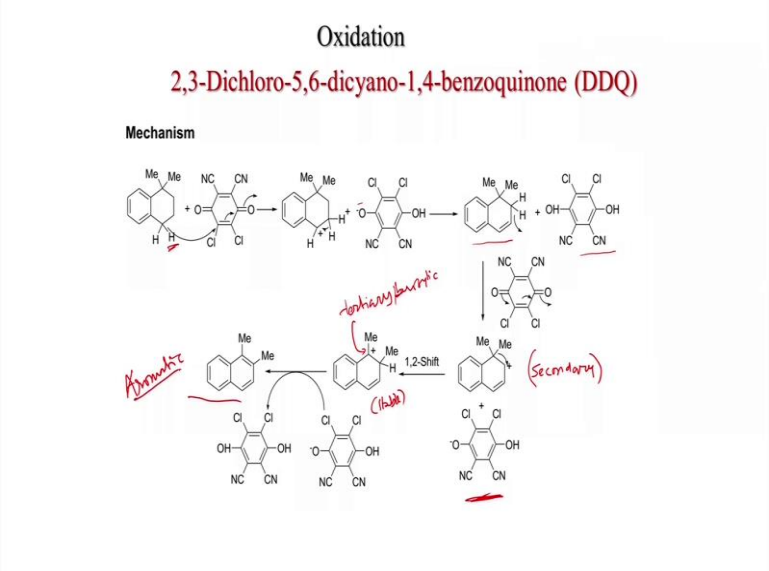

Now we will discuss how this reaction operates. So as I told that one H minus will first react. So one H minus, because this is benzylic, so benzylic carbocation is stable so H is quite acidic, so H minus, H minus will react and there will be, carbocation formation will be there. So carbocation formation will be there and H minus can react either here or here, whatever.

It will give the same product and if it reacts here and then after tautomerization, you get this compound O minus, and H here. So O minus is generated and now this O minus will react with one hydrogen here, because this is carbocation so this will, like we have seen the olefin formation so this H plus will be taken by the O minus and you get this compound now, neutral compound hydroquinone and this compound is formed. So a double bond has generated.

Now again one H minus will react because this will be allylic carbocation, that is also quite stable. So H minus will come again to this compound DDQ and again it will react either here or here, it will generate again a O minus here. And now this compound, this carbocation, after this carbocation, if you see this is allylic but this is a secondary carbocation.

And we know that if there is a possibility of a carbocation rearrangement. If the carbocation wants to get stabilized like from primary to secondary, secondary to tertiary that process is very facile and that's what is happening here. Here after 1 to 2 methyl migration, the carbocation goes to here. And this carbocation you can see this is a tertiary carbocation, tertiary carbocation as well as benzylic, so this is quite stable.

So this carbocation is stable so this 1 to ethyl migration is very facile. You get this carbocation and then this O minus will take up this H plus and you will get the olefin, ultimately you get the aromatic compound. And your di hydroquinone becomes this, sorry DDQ becomes this dihydroquinone.

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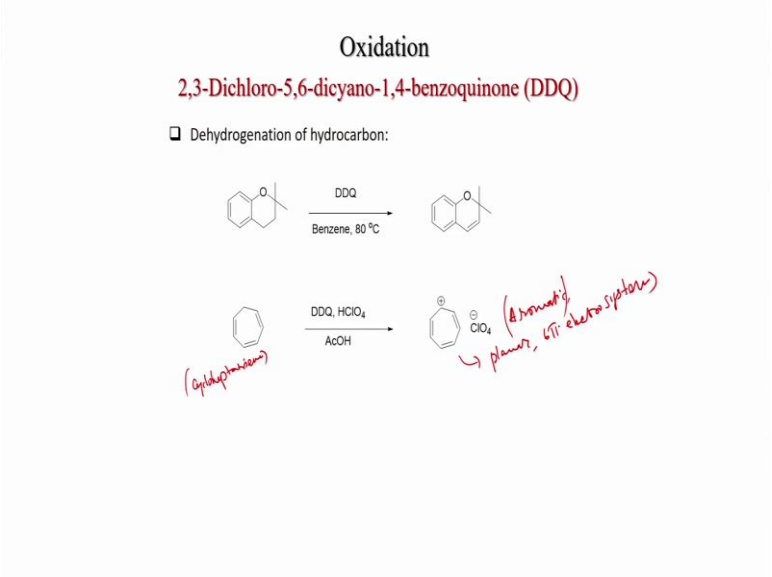

Similarly DDQ performs dehydrogenation of hydrocarbons like this chroman system. Here two methyl groups are there. So it cannot aromatize. So only one single double bond is formed when DDQ and benzene 80 degrees Centigrade we do the reaction. Also cyclo heptatriene system and we know that this is not aromatic but if you generate carbocation and this is very quickly possible if you treat DDQ, $HClO_4$ acetic acid.

This you get the carbocation and this is aromatic because this is planar, 6 π electron system. So this is aromatic and so this procedure is very facile. Also if you have a system like this, then also under this condition DDQ sodium nitrate condition, you can get the double bond here and this is also the room temperature you can do this reaction.

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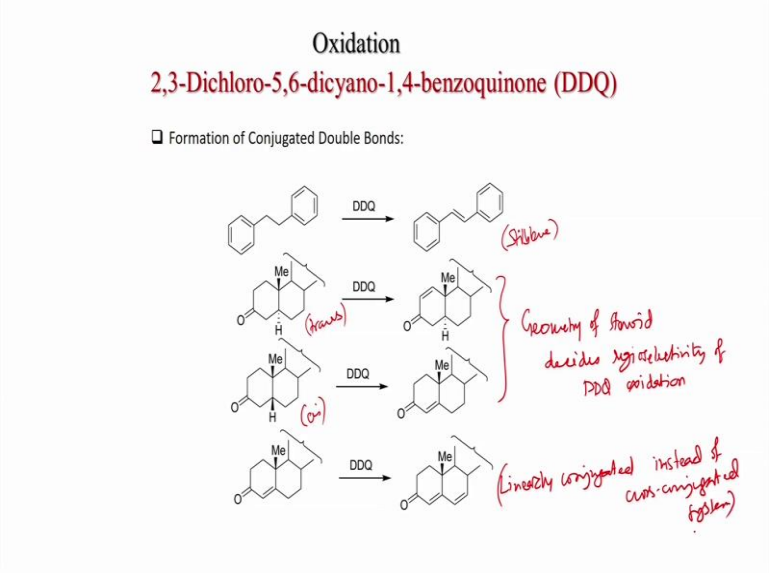

DDQ also forms conjugated double bond. This is very usual reaction of DDQ and if you have possible of conjugation then it is very facile. Like if you have system like this, diphenyl and intermediate is this, that is the hydrostilbene actually, dihydrostilbene, and then you get the stilbene.

So DDQ generates the stilbene and this is very interesting that if you have a trans steroid, so these are steroid compound, this we will see the mechanism later also, in a trans system you get dehydrogenation from this side. And in cis system you get dehydrogenation from the, this side.

So this is the geometry of steroid decides regioselectivity of unsaturation, regioselectivity of DDQ oxidation. So it is the geometry of the steroid. If it is trans then this side is cis this side and also there is already one unsaturation here then it does not go this side. In fact it goes to this side, so linearly conjugated system. This is linearly conjugated instead of cross conjugated system. So in this case, a linearly conjugated system is generated compared to the cross conjugated system.

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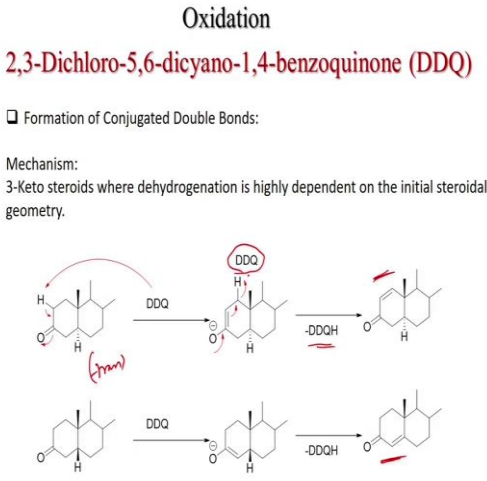

Formation of conjugated double bonds, so this is mechanism that we told the three keto steroids are there, highly dependent on initial steroid geometry. So when it is trans then it has been found that this, this enolate will form and after this enolate, after this enolate then you get this hydrate, hydrate elimination for this hydrogen and you get, after elimination of DDQH, you get this double bond, alpha beta unsaturated carbonyl system.

And in cis system now this enolate is formed and after that you get oxidation of this one. So you get this carbon and when trans case, you get this carbon. So this will be the accessibility. Which hydride and H plus is accessible? So there, depending because here this H minus will react with DDQ and here this also will react with DDQ. So this is very important that accessibility of the hydrogen to DDQ and that is why the facial selectivity operates here.

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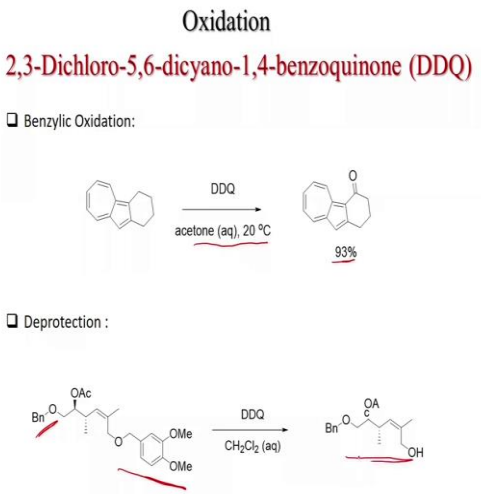

Benzylic oxidation, DDQ also has been found to do benzylic oxidation like this system. In acetone 20 degree Centigrade, you get 93 percent yield. This is allylic system, you get the carbonyl here and it has been used also, benzylic deprotection. Like here simple benzylic group is there but here activated 3, 4 dimethoxy system is there.

And when DDQ in dichloromethane aqueous, dichloromethane was treated with this substrate, you get deprotection, you will get this allylic alcohol. So this benzyl group still remains so this is very important. Then this group is more electron rich so it has a chance to more react with the DDQ.

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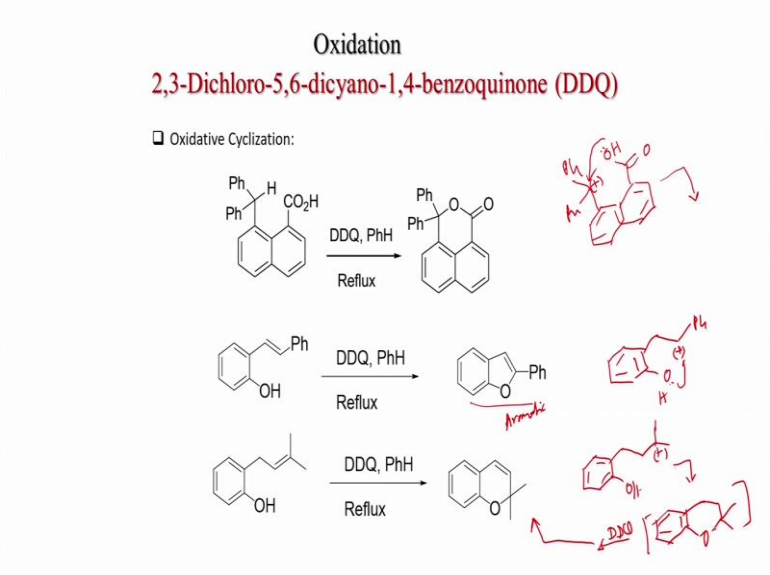

Oxidative cyclization, DDQ also used in oxidative cyclization reaction. If you see this compound there is a benzydrylic carbon here and with DDQ condition you get the cyclization. So what is happening? This is a carbocation that is what we told earlier, with ceric ammonium nitrate.

Here also you get a carbocation, carbocation and this, this is reacting with the carboxylic acid, may be the anion of the carboxylic acid and you get this compound because this is 6-member ring formation, so this is quire facile. When you have an olefin here and then also the 5-member ring will form, the most likely, this goes where?

This carbocation, so this electron reacts with DDQ and then generate a carbocation here and then it is reacting and then after dehydrogenation, because DDQ also dehydrogenation, and

then you get this aromatic system. And this compound, it has been found that when it cyclizes then the double bond isomerized, the double bond isomerized and you get this 6-member ring.

So here also first this carbocation will form. As this carbocation will form and then it will go to this compound. And then as we have seen that DDQ dehydrogenates so this product, this product or intermediate will be converted through this product. So the cyclization will happen because this electron cloud will react with DDQ to generate carbocation and then cyclization and then again dehydrogenation will give this compound.

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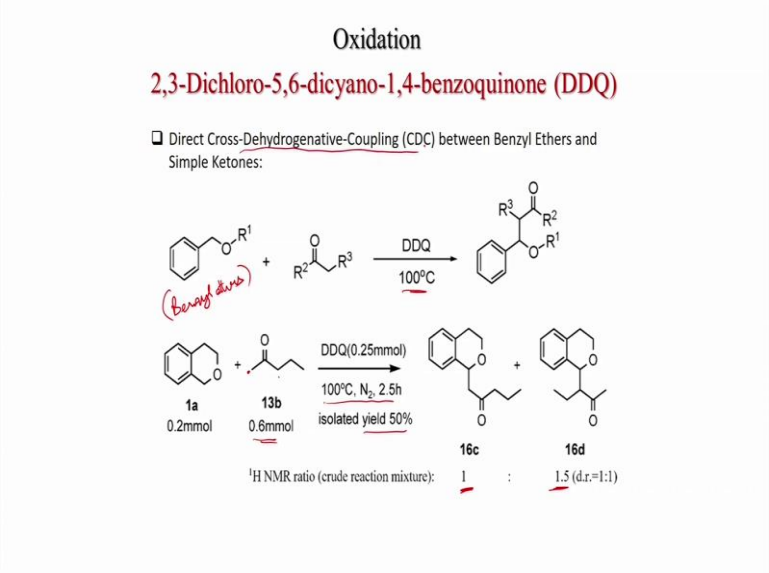

Direct cross dehydrogenative coupling between benzyl ethers and simple ketones, benzyl, this is benzyl ethers, and ketones, it can give this reaction. So alpha position of ketone, because the enolate formation happens and then it reacts with the oxonium R. So detail mechanism we will see and this condition is DDQ 100 degrees centigrade.

Suppose if you do this reaction chroman and 2 butanone, 2 butanone in 3 equivalent and DDQ, this is anhydrous solution 100 degree Centigrade nitrogen atmosphere 2.5 hours isolated it 50 percent you will get a mixture of products. So ketones, 2 positions are there, this is primary, this is secondary. Here it has been found the secondary that product is more in 1.5 and this is 1 ratio. But main thing is that C-C bond formation happens. So this, that is why this is called also cross dehydrogenative coupling.

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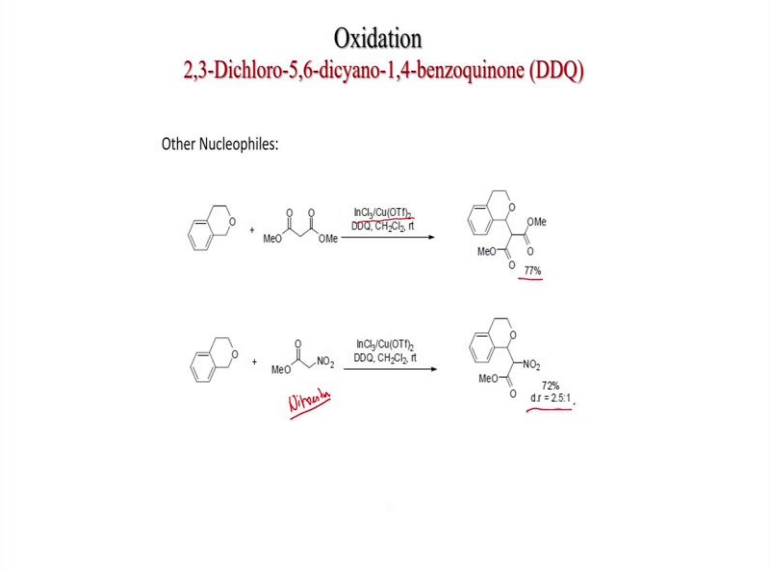

Other nucleophiles can also be used in this reaction to the chroman and like dimethyl malonate can be reacted with chroman. You have to use other Lewis acid along with DDQ in room temperature, you will get 77 percent yield of this product. So here also you will get oxynium ion and then this negative charge of dimethyl malonate, this reacts here and you get this product. Here also this is activated nucleophile nitro esters, and this nitro ester, nitro ester under this condition, indium chloride copper triflate which acts as Lewis acid and DDQ, you get these products in, dr ratio 2.5 is to 1.

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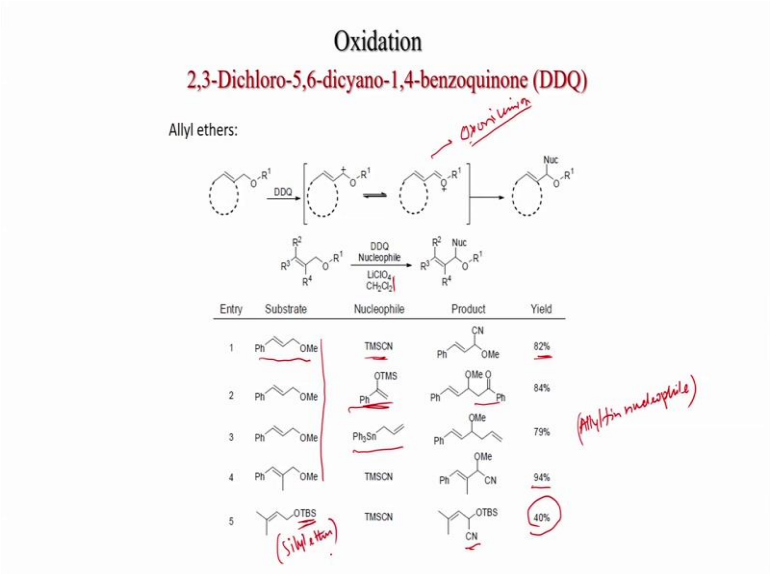

Not only benzylic ethers, allylic ethers can also be reacted under this condition. So DDQ you have to use lithium chloride here. DDQ, lithium chloride and dichloromethane solvent you can get the carbocation fast than the oxonium, so this is the oxonium ion and then a

nucleophile can be reacted. As you can see, this is the allylic ethers. This is the formation of carbocation here and this hydride will be taken by DDQ and DDQ then the oxonium ion will generate and you get reaction with TMS cyanide, you get 82 percent yield.

Similarly in allyl ether, OTMS silyl ether can react to get this ketone. Similarly allyl nucleophile, allyltin nucleophile can be reacted with this allyl ether to get this product in 79 percent yield. Similarly if there is a branch also, the reaction is possible. So the branching does not affect the oxonium ion formation and you get 94 percent yield.

Also if this is OTBS, not only methyl, this is one methyl here, OTBS, this is also possible. So the silyl does not affect the oxonium ion formation here and you get the oxonium and then cyanide. However the yield gets reduced. So methyl ether are better choices compared to the silyl ethers.

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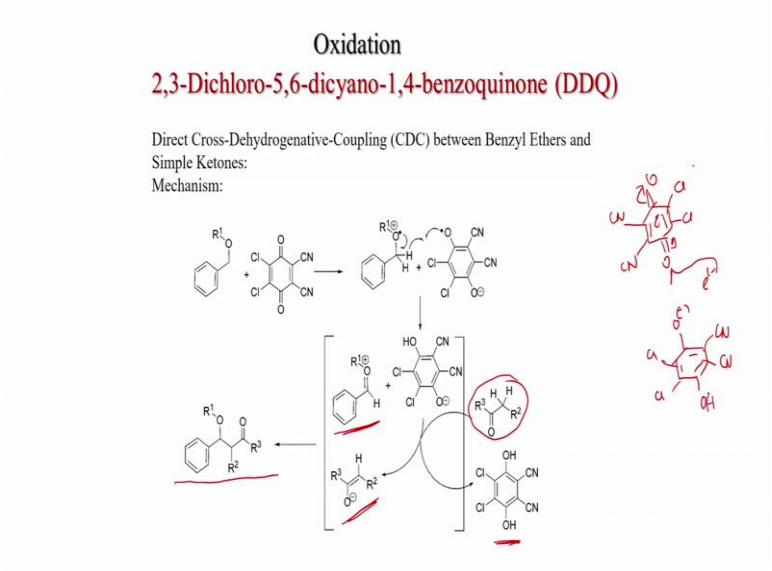

Direct cross dehydrogenative coupling between benzyl ethers and simple ketones, so this is the mechanism that benzylic ether, this oxygen, there is a lone pair and we can think that first one electron goes from the oxygen lone pair to this DDQ and you get a radical here because if you see this structure and the electron if it comes here, then single electron then, the radical will form here, O radical and O minus here, so this will be radical.

And what happens? Now again this H dot will go to this O dot and it will give the OH, and because there are two radical, now bond will form so oxonium ion will form. And you get the anion. Now this goes to OH and this you get CN, CN, Cl, Cl and this O minus then reacts

with the ketone. So this O minus reacts with the ketone to generate the enolate. and this already is oxonium ion.

So DDQ activating both electrophile and nucleophile, both partners, this as well as the carbonyl compound, this both activated by DDQ, so this enolate is forming where this is the base now and after deprotonation it becomes the hydroquinone system and now this is an oxonium ion, this is an enolate, so this reaction will take place, desired reaction and you will get the C-C bond formation.

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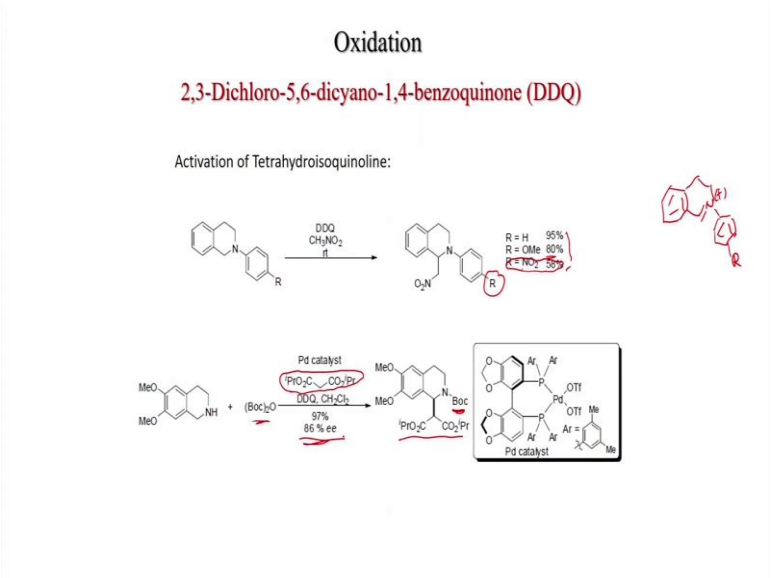

Activation of tetrahydro isoquinoline not only chroman, but quinoline system also, isoquinoline system can also be reacted under DDQ, so DDQ nitro methane solvent room temperature, if you have the N Phenyl system you can get reactionary nitromethane. So C-C bond formation. Here also mechanism most likely iminium ion is formed. So first one electron, then another electron oxidation and then you can get the iminium ion.

And it has been seen, it has been observed this, that the iminium ion is forming, actually that also can be observed by changing the R group. Suppose when hydrogen is there 95 percent, methoxy 95 percent, 80 percent and when R is equal to NO_2 then you get 58 percent. So if there is electron withdrawing group then the iminium ion is destabilized.

And this is chiral version with ceric ammonium nitrate and chiral ligand and palladium catalyst, so this is the phosphene ligand and pallidium triflate is there and under this condition

is Boc anhydride and dimethyl, di isopropyl malonate is acting as a nucleophile and you get this product. Here, the Boc group is required otherwise this reaction will be reversible.

So if you put Boc anhydride under this condition, Boc protection is happening and you get this product in 86 percent enantiomeric excess. So this is very important that ceric ammonium nitrate can generate the iminium ion and then the chiral catalyst will do the facial selectivity so that one face is blocked of the iminium ion and you can get the addition from the selective one face to get a chiral or enantiomerically enriched product.

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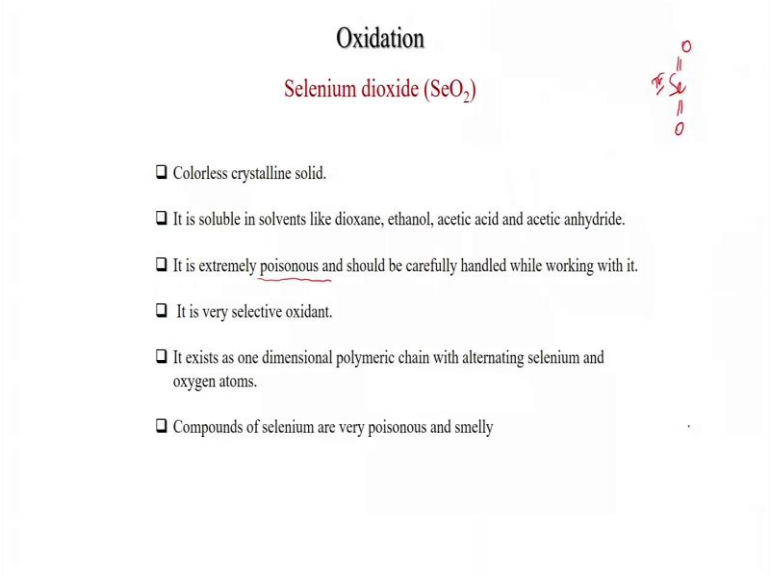

Now we will discuss another oxidizing agent which is selenium dioxide. So this is selenium dioxide. Selenium is 4, we know that oxygen sulphur selenium, it is in that series, so it is colorless crystalline solid. It is soluble in solvents like dioxane, ethanol, acetic acid and acidic anhydride. It is extremely poisonous and should be carefully handled while working with it. It is very selective oxidant. It exists as one dimensional polymeric chain with alternative selenium and oxygen atoms. Compounds of selenium are very poisonous and smelly so you have to handle carefully.

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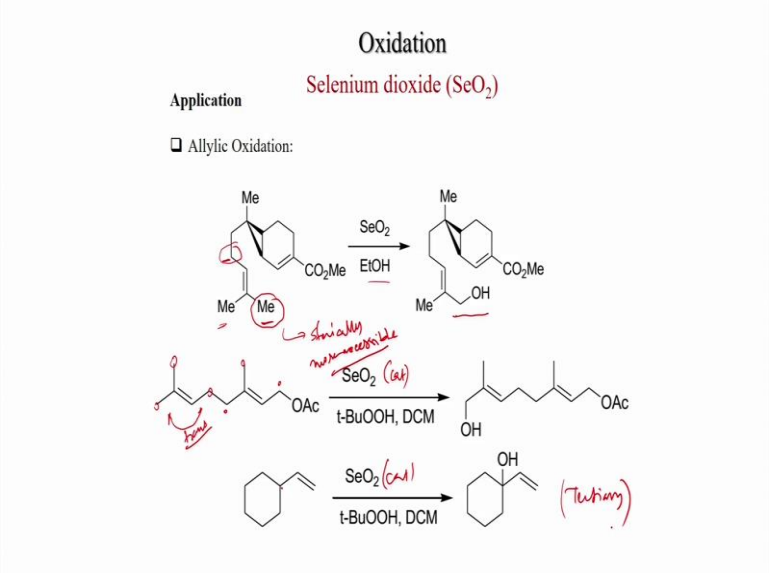

Selenium dioxide, one major application is the allylic oxidation. Like this allylic system there are three allylic carbon is there, this methyl, this methyl and this CH_2 group and if you put selenium dioxide in ethanol, you get selectively this; methyl is going to the CH_2OH group. So this is very important. So the group which is getting oxidized, which is trans to this group, so what means, it means that it is sterically more accessible.

So the methyl group which is more sterically accessible is getting oxidized to the OH. This methyl is getting oxidized to the allylic alcohol. And here also you can see this is geranyl acetate, selenium dioxide here it is catalytic amount and tertiary butyl hydroperoxide, it is the stoichiometric amount in dichloromethane solvent.

There are many allylic carbon, this, this, this, this, this, this so selectively only one allylic carbon is getting oxidized with selenium dioxide, that is this methyl group which is also trans to this, it is trans to each other. That means sterically which is more accessible, that is sterically less hindered, that carbon atom will get oxidized. And here you can see only one allylic carbon is there.

So that is why tertiary alcohol is generated here. So when there is no other opportunity, only one carbon is allylic. That case only one product will form. So you get this tertiary alcohol under selenium dioxide catalytic amount and tertiary butyl hydroperoxide stoichiometric amount.

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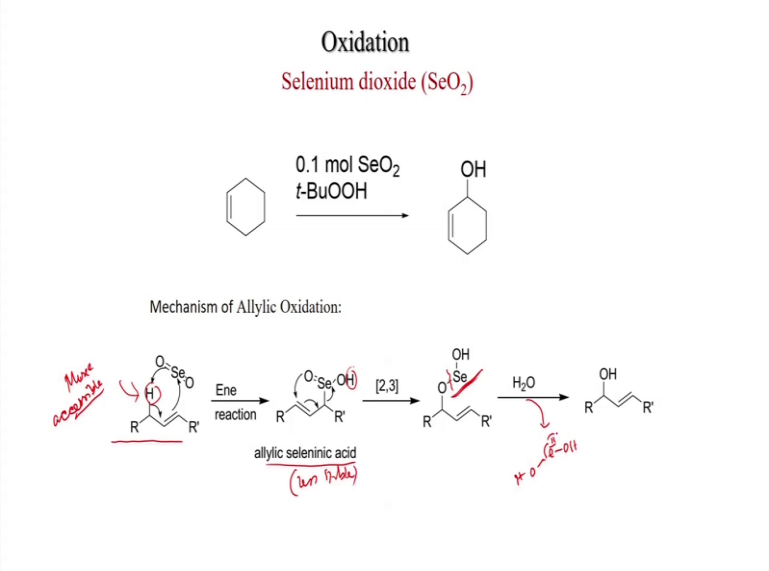

Here cyclohexane is used and cyclohexanol is formed. You can see 0.1 mole of selenium dioxide and tertiary butyl hydroperoxide. This is the mechanism of this allylic oxidation. So what happens, this allylic CH, this CH which is more accessible, this reacts with this oxygen here and now this double bond migrates so this is ene kind of reaction and you get reaction here and this hydrogen is this hydrogen. So this hydrogen is going to here with the oxygen and you get selenium carbon bond here, and which is not very stable.

So that is why, again 2,3-sigmatropic rearrangement is happen. So this is allylic seleninic acid less stable. Now again oxygen is reacting here and you get this carbon silicon bond breakage and you get this compound. And this compound if you hydrolyze what will happen? This bond will break and you will get SeOH SeOH, so this becomes 2. So selenium 4 becomes 2 and you get the allylic alcohol. So two times rearrangement of the double bond keeps the double bond in the same place, first in the ene reaction and then 2, 3 sigmatropic rearrangement.

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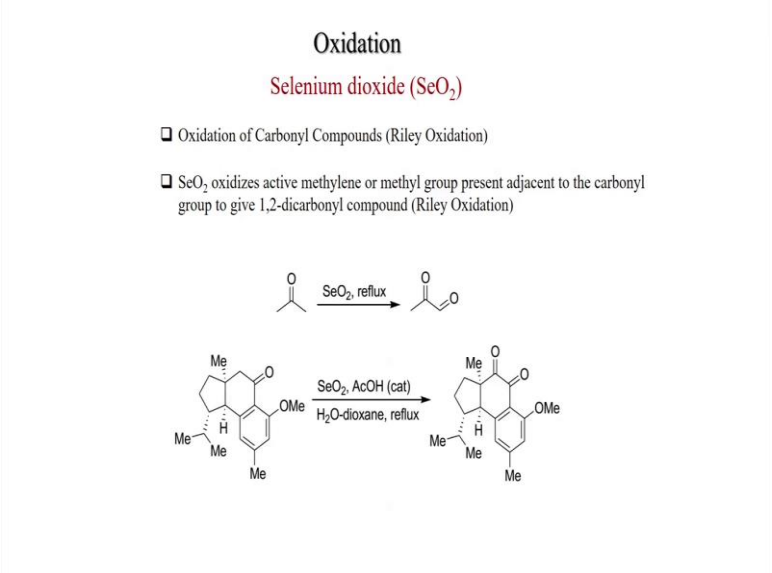

Oxidation of carbonyl compounds which is Riley oxidation also called, SeO_2 oxidizes active methylene or methyl group agent present adjacent to the carbonyl group to give 1,2-dicarbonyl compound. This is also very popular reaction of selenium dioxide. As you can see, here acetone with selenium dioxide reflux condition gives this keto aldehyde and this is an intermediate Hamigeran B. Mehta group did this reaction and selectively this carbon is getting because this is alpha to the carbonyl. Under this condition selenium dioxide acetic acid catalyst H_2O dioxane, reflux you get this 1, 2 keto system which has intermediate for Hamigeran B synthesis.

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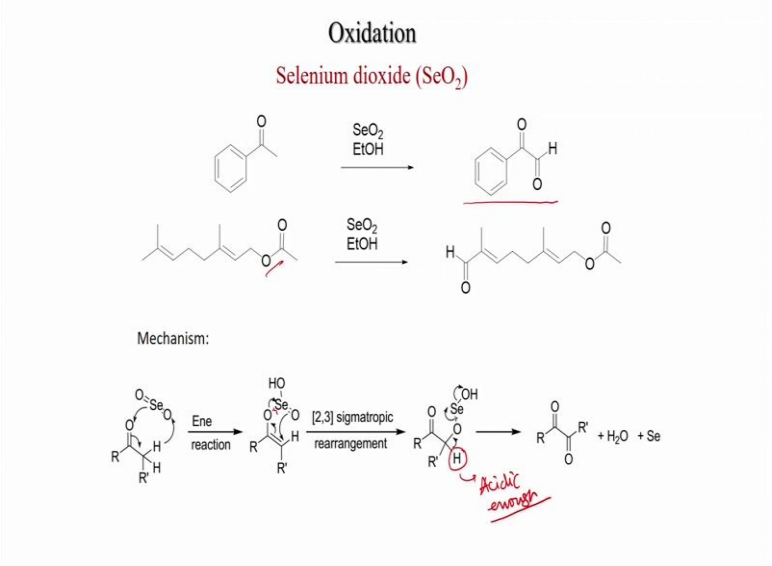

Also acetophenone can be reacted with this selenium dioxide ethanol. You get the keto aldehyde, that is the alpha to the carbonyl going to the carbonyl group and here there is no

carbonyl group. Only the ester is there, but this is unreacted. Only under this condition this allylic goes to the first alcohol and then it goes to the aldehyde. So what is the possible mechanism for this reaction?

So here also this hydrogen will react, this hydrogen is acidic and this will react to the oxygen. It will go to the oxygen to make OH and this selenium will make a bond here with the carbonyl group so you get this Ene reaction. This is also Ene reaction. That selenium reacts with the carbonyl and hydrogen goes to the oxygen and you get oxygen silicon bond. Again 2, 3 sigmatropic rearrangement, 2, 3 sigmatropic rearrangement generate this one. This oxygen now react here and you get O silicon bond breakage. So this bond is breaking to make another O silicon bond.

So earlier what we have seen that this kind of system, if you give the water or the water present in the solvent hydrolyzes this bond, but in this case what is found that this proton, this is quite acidic because this is alpha to carbonyl. So this is quite acidic enough. This is quite acidic enough to get eliminate and you generate this carbonyl here and this oxygen silicon bond breaks like this.

So you get a carbonyl group here, carbonyl group is generated. Not only earlier what we have seen the allylic alcohol generation only this bond breaks but here this hydrogen is acidic enough so that rearrangement happens that the carbonyl is generated and you get H_2O and selenium. Instead of SeOH, here selenium zero is formed. So allylic oxidation we have seen, SeOH whole 2 is forming but here selenium zero is forming.

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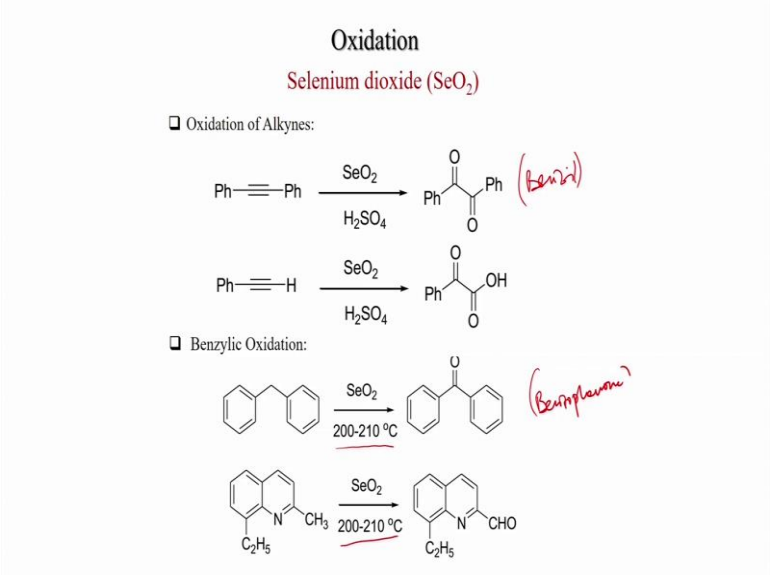

Selenium dioxide also has been used to oxidation of alkynes like this compound is converted to benzyl in selenium dioxide H_2SO_4. Also phenyl acetylene is converted when selenium dioxide H_2SO_4 to the keto carboxylic acid, benzylic oxidation can also be performed with selenium dioxide. Only you need very high temperature so 200 to 210 degree Centigrade, under this condition you can oxidize the benzylic group.

We have seen that in DDQ condition, even in CAN also but here selenium dioxide can also oxidize benzylic carbon to a keto group. So here benzophenone is forming and here this methyl group is getting oxidized to the aldehyde group with selenium dioxide condition.

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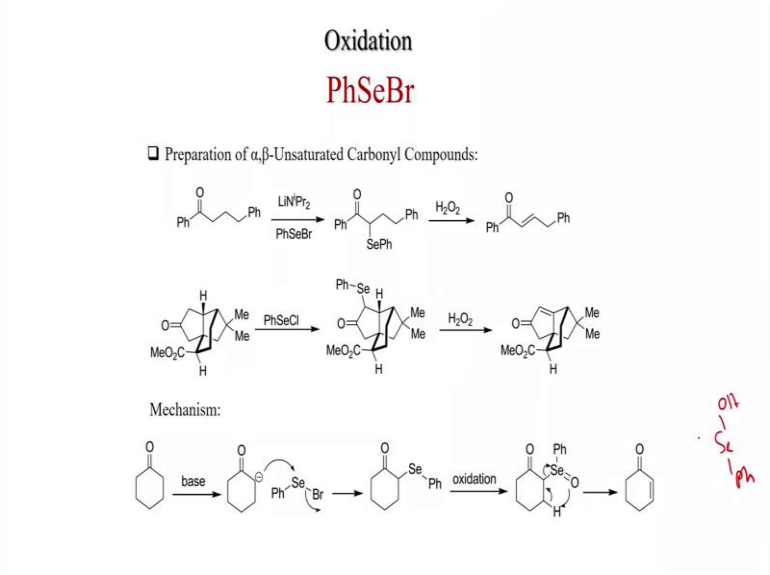

So another reagent that has been used which is phenyl selenium bromide, this is preparation of alpha beta unsaturated carbonyl compounds. So if you have the ketone then with base and phenyl selenium bromide you get the alpha functionalization of alpha selenium compound and then with H_2O_2 you get the alpha beta unsaturation here. So this reaction also is popular and it has been used in many natural product synthesis. Here is one of the complex molecule with a carbonyl compound and when it was treated with phenyl selenium chloride you get this carbon selenium bond and this, when treated with H_2O_2 it becomes alpha beta unsaturated carbonyl.

So we will discuss the mechanism here. As you can see here first, base generates an enolate. Then enolate reacts with phenyl selenium bromide to give this alpha selenium ketone and then oxidation happens of selenium to get the selenium oxide here. And then the elimination happens of the carbon selenium bond breaks and under this condition you get the olefin. And what byproduct is, Se(OH)Ph so this is the byproduct of this reaction. So today we have discussed three oxidizing reagents.

First one was the ceric ammonium nitrate. We have seen ceric ammonium nitrate oxidize secondary alcohol compared to primary alcohols. It also open aziridine oxidative reaction that amino ketone you can get. Also epoxide also it opened and you can get the keto alcohol, also benzylic carbon also can be oxidized. And with DDQ, DDQ mainly does the unsaturation. We have seen it helps in aromatization, alpha beta unsaturated carbonyl compound, also cross dehydrogenative coupling also it has been used. It has been used to activate chroman, also tetrahydroisoquinoline.

Also we have seen that oxidative cyclization reaction also it has done and you can get, if phenolic oxygen is there then you can do the cyclization. And now selenium dioxide, very popular for activating allylic methyl group and the methyl group which is more accessible, less sterically crowded. Generally trans to a carbon atom that methyl group selectively oxidized with selenium dioxide to give alcohol. And when the carbonyl compound is there then also selenium dioxide, this is special of selenium dioxide; it can give 1, 2 dicarbonyl compound. Thank you.