Molecular Rearrangements and Reactive Intermediates in Organic Synthesis

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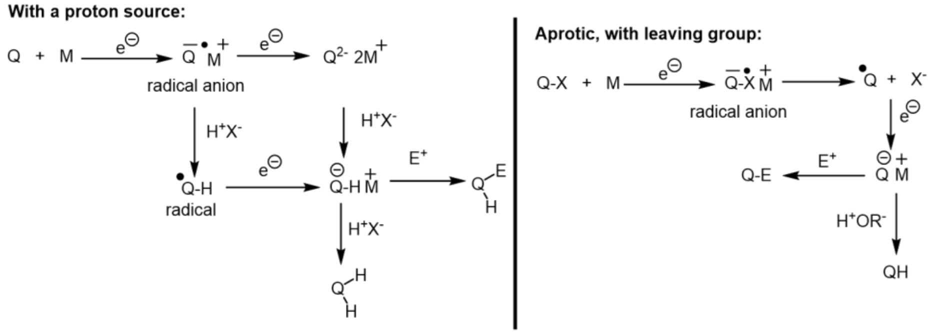
Lecture 22: Free Radical Continued

Welcome back to this NPTEL online certification course in molecular rearrangement and reactive intermediates. In the last couple of classes I was talking about the radical chemistry. I talked about the different types of methods of generational radicals and their different type of name reactions. In the today's class I decided to talk about some of the single electron transfer reaction. So, in the today's class topic I am going to talk about the reduction using metal-based reducing agent. So, I am going to talk about lot of the single electron reduction using the sodium, potassium, magnesium.

And, then also the acyloin condensation, another very important name reactions, then the the Bouvault-Blanc reduction and then finally, the very important Birch reduction. So, before I go to all these different chemistries first, I want to start with this the basis of this metal-reducing agent. what is the general reactions, and how this reaction happens. generally, you can see that there are a number of metals at the zero or low oxidation states.

we are talking about some sort of a the metal like the sodium, lithium, potassium, magnesium and zinc. we are also going to talk about some titanium and samarium. So, you will see that in a separate class, we are going to talk about some of the reactions of samarium. So, here what is happening with these these are low-valent metals, which can give a single electron. So, it is actually act as a reducing agent and then you can see several different type of chemistry. So, these are called electron transfer agents . So, what is the mechanism? if you have a proton source then what is happening? the metal first is giving one electron to this Q . So, that is becoming a Q radical anion and M+. So, this is a radical anion formation happening.

A number of metals at the zero or low oxidation state that readily donate **one or more electrons** to molecules with an accessible LUMO orbital (Li°, Na°, K°, Zn°, Mg°, Ca°, Cr^{+2}, Ti°, Sm^{+2}, etc) can reduce a molecule is known as **electron transfer reagents**.



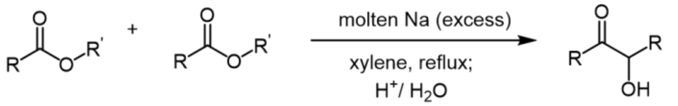
After that, if you have an H+ and X-, then the Q-radical anion now takes the H+, and then it becomes QH. So, it is a radical with the proton, and if you take one more electron from this, then it will become a $[QH]^-$ M^+ because now sodium will be plus, which can take another HX to form the QH_2. or if you have an electrophile, then it can become this QEH. Of course, we are going to talk about several different electrophiles in the class. If you have a aprotic solvent with a leaving group then what is going to happen.

of course, now you are starting with QX. So, here you started with a QX because X is a leaving group. again, if you give a single electron, then what is going to happen is there will be a heterolytic cleavage of this QX. here you can see there is a radical anion is going to form here, and now you can form a Q• and a X^-. So, as I said there will be heterolytic cleavage and then if you give one more electron then the Q• will become Q^-.

it will take a proton at the end to form a QH or if you take an electrophile to become QE. So, these are the two different scenarios I am going to explain to you. In one case, you have seen that there is no leaving group. In one case, you have a leaving group like a QS. So, let us now come to a real example.

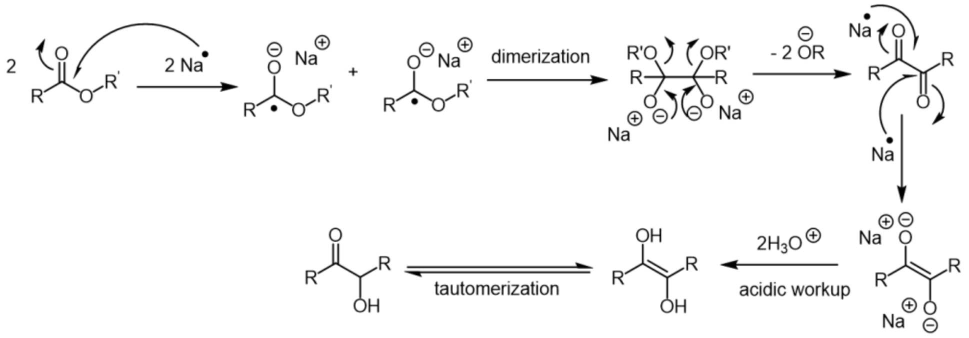
So, the first reaction I am going to talk about is a acyloin condensation it is a bimolecular. So, the I think every single term is very important here this is a bimolecular. that means two of these esters is going to form a bond. then, this is a reductive coupling, which means the reduction is happening between two carboxylic esters and one important compound, an alpha hydroxy ketone. So, this is a bimolecular reductive coupling between two carboxylic esters, in presence of molten sodium in excess and xylene in refluxing condition and then you quench the reaction and forming a very important compound called α-hydroxy ketone.

Bimolecular reductive coupling between two carboxylic esters in aprotic solvents like, xylene, toluene, benzene, ether Known as **acyloin condensation**.

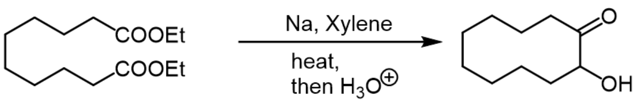


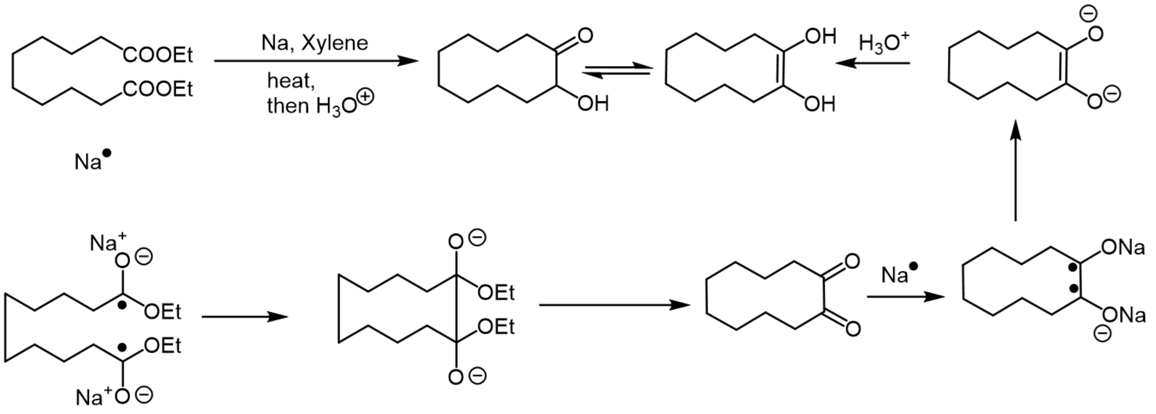
α-hydroxyl ketone

Mechanism:



So, let us try to understand the mechanism. So, before I go to the mechanism, one thing we should try to understand that where this single electron transfer is happening. Suppose if it is trying to reduce this carbon-oxygen bond then where the single electron is coming in. Of course, the single electron is given to the corresponding LUMO orbital. Suppose if you have a carbon-carbon bond; let us try to understand why. So, we are going to really try to focus on this first step. that once you have this ester and once the sodium gives single electron, you end up forming this carbon• and O$^-$. Why this is happening? Of course, in the textbook, you might say that this oxygen is more electronegative that is why oxygen will be the minus and then carbon will be the dot, but how this is coming into the picture. So, if you try to understand that particular thing, you have to go to the the bonding orbital. So, if you think about carbon-carbon single bond.





So, two of the carbon forming a bonding and anti bonding. Of course, they have bonding electrons, and we can say this is a bonding and this is an antibonding. One of the important things is these two carbons are actually in the same energy, but once you have carbon and oxygen, then because oxygen is more electronegative, it is going to stabilize it. So, now, your oxygen is here in and the carbon is here. Now, if this is your bonding, anti-bonding, or the HOMO, LUMO, whatever way you want to say them, and if they are forming a bond Now, if this is your bonding and this is your anti bonding then your homo of this bond actually close to the oxygen not the carbon .

So, that is a very important thing here that is why when you are giving one more electron. So, the electron coming from sodium to the corresponding anti bonding orbital . So, that means, you can clearly see the HOMO is close to the oxygen the LUMO is close to the carbon. That is why, after the first reduction happens, you see oxygen has 2 electrons, which is why the O- here and then carbon have this dot. I think you understand this part now.

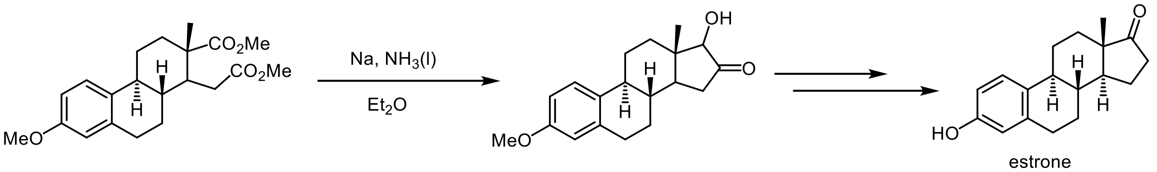
So, now what is happening, this is a bimolecular reaction happening. So, sodium is reducing the ester, forming this in C• and O-, there will be another one another ester also after taking one electron it is going to form that. So, now two of this can form a dimer. we already talk about that the radical can form a dimer. Radical dimerization is a reaction that I have already discussed before.

So, this is a dimer formation happening first. Once the dimer formation happening, next thing is you have a leaving group here. you have this. So, now, if you see there is an O- and OR. every carbon, you will see O- and OR.

So, this O- is going to come back and get rid of this OR. So, you can see in this particular step 2 equivalent of alkoxide is actually coming out. after one or two slides, I am going to explain there is a problem with that because you are generating 2 equivalents of alkoxide that can do other side reactions. But again, once you form this 1,2 dicarbonyl compound the reaction is not going to stop here. because your carbonyls are even going to take the single electron from the sodium and going to be reduced further.

So, sodium will going to give one electron here. both of this carbon going to form the dot here which can form this compound in the acidic workup. finally, you come to here and then after the tautomerization you will going to form the corresponding α-hydroxyketone. So, first thing is the dimerisation of the 1,2-dicarbonyl compound .1,2 -diketone further reduction to the alpha hydroxycarbonyl compound.

Again here is an example. mostly you will see these reactions are going to be used for the formation of the ring. you have 2 esters here. they are participating in acyloin condensation in presence of sodium and xylene, going to form this compound here which is again you can see a α-hydroxy carbonyl compounds, you are forming at the end. again if you see the mechanism, it is very similar mechanism. first thing is the reduction of the ester with a single electron, forming a C• and O^- with Na^+.



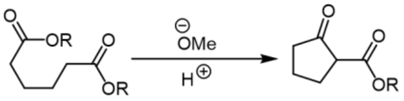
Again, very similar thing happen then the radical going to recombine. After that alkoxide going to get out from here and then forming 1,2- dicarbonyl compound again the sodium is going to transfer one more electron. So, two of the sodium will transfer one , one electron here to reduce them. then finally, after the the protonation it is going to end up forming this corresponding product . So, you can see there are several example.

I just included one example here. you can practice more and more examples from the literature. Another important example is here. you can see there are two esters now. These two esters are again going to take part in the acyloin condensation in the presence of sodium and liquid ammonia and in presence of diethyl ether.

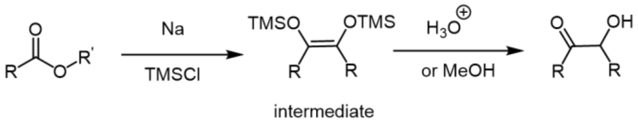
what is going to happen? you again end up forming this α-hydroxy carbonyl compound. I think the mechanism I already have discussed. a very similar mechanism is happening. first single electron transfer to form C•, followed by the radical recombination then get rid of the alkoxide to form 1,2- di-carbonyl formation. then further reduction can form the corresponding α- hydroxy ketone, which can be finally converted to estrone.

And then I think I already talked about that, in this reaction you are getting rid of 2 alkoxide ion. Again alkoxide are strong enough so it can able to deprotonate. That means, if you have an alkoxide base in the medium, which is coming out, it can able to deprotonate from the ester. So, the α-proton, which is α to the ester, is going to get deprotonated, and you can write in some sort of O^- and so after this, there will be a double bond O^- and then this can come back, and now this enolate, an attack to another ester. So, this is the intramolecular cyclization called Dieckmann condensation.

- The reaction also produces **stoichiometric quantities of alkoxide base**, which can catalyze the competing **Dieckmann condensation**



- In recent methods TMSCl has been used to remove alkoxide ions from the medium thereby preventing base catalyzed side reaction

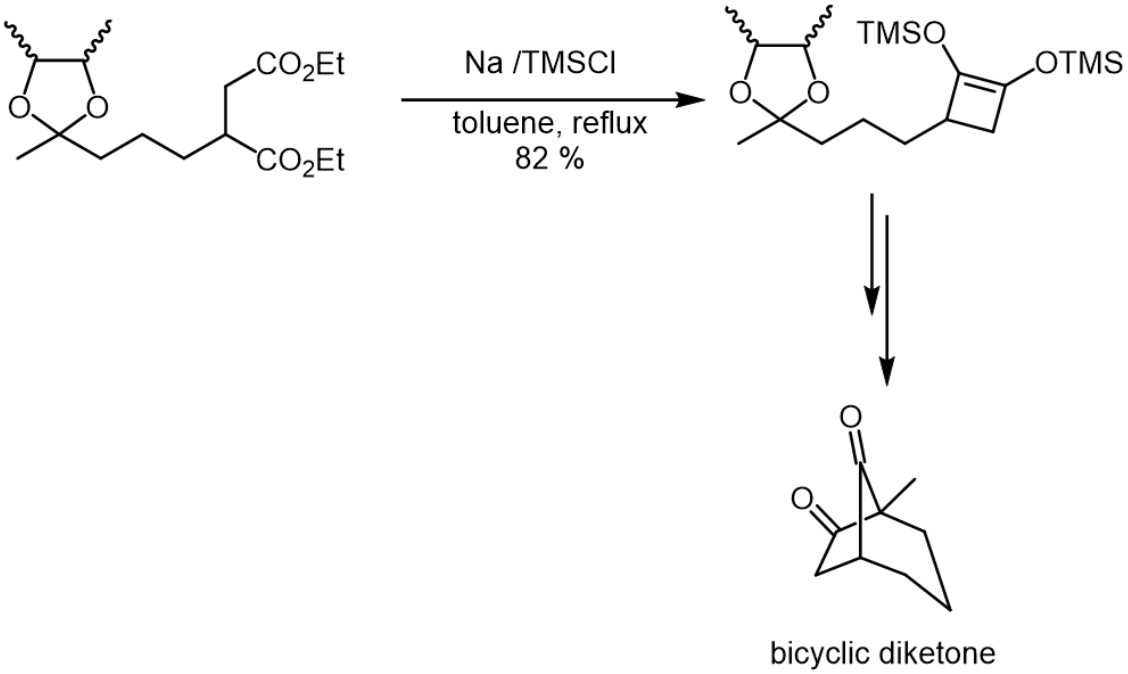


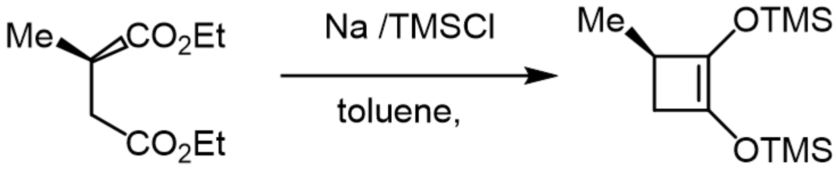
So, this can happen. So, this can be a byproduct in this reaction,because you have a 2 equivalent of alkoxide base coming out. So, to stop that, they thought of not using alkoxide, or use some other way to get rid of alkoxide. I think the other way is how to remove alkoxide ions from the medium. That is the technique they used. They want to get rid of the alkoxide using TMS chloride.

That means, once you have this ester here. you are using sodium and TMS chloride. now what is happening? your intermediate is now becoming OTMS. then what is going to happen? then if you use the H_2O^+ and methanol, it is going to form the corresponding α-hydroxy carbonyl compound.

So, here is what is going to happen. that you are removing the alkoxide ion from the medium by using TMS chloride. So, that is one of the tricks you can use. So, that now you have this OTMS formation happening, which can be easily going to form the corresponding α-hydroxy carbonyl compound. Again, there is an example here, of course; you are now using the TMS chloride. So, you are forming this corresponding OTMS here, which can be going to form the bicyclic ketone here.

There is another example, you have the sodium and TMS chloride. So, that can again form this very similar intermediate here the OTMS and now if you do not quench here, you can isolate in this stage, but now if you use a H_3O^+, you end up forming the corresponding α-hydroxy carbonyl compound.

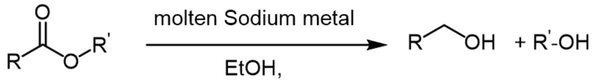




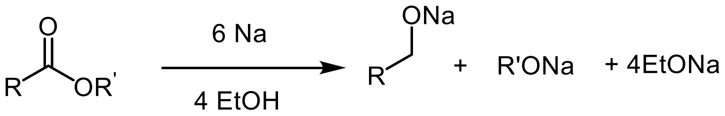
So, now in the previous slides what I was talking about is that, when you performing the acyloin condensation if you have a protic solvent. So, in the previous case ,if you see in the reaction, we talk about xylene, we have not talked about any type of protic solvent; we talk about xylene with molten sodium. And then of course, once the reaction is over, now you are quenching with the H_2O to get to the product.

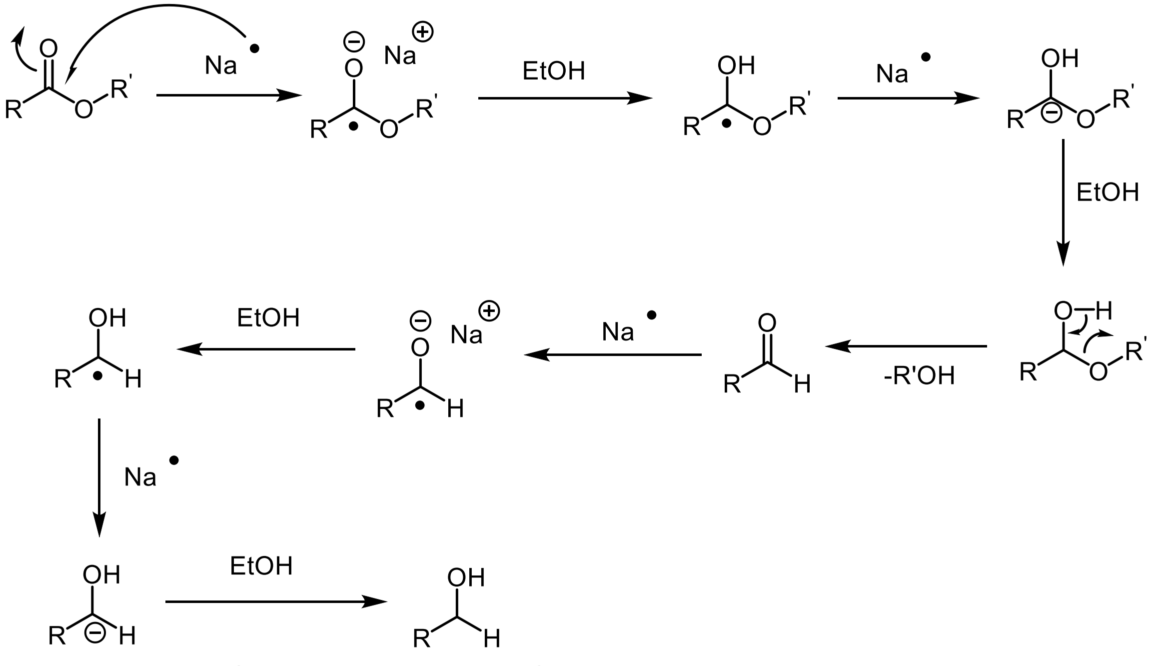
But the question comes if you use ethanol as the solvent in this reaction what is going to happen? Because if there is an alcohol present, then, instead of forming the corresponding α-hydroxy ketone, you end up forming a corresponding alcohol after the reduction of the ester. So, there will be reduction of ester going to take place and that is called the Bouveault- Blank ester reduction reaction.

- The reaction is performed in aprotic solvents with a high boiling point, such as benzene and toluene, in an oxygen-free atmosphere (as even traces of oxygen interfere with the reaction path and reduce the yield). **Protic solvents** effect the **Bouveault-Blanc ester reduction** rather than condensation.



So, now, we try to understand the mechanism of this reaction. of course, we know the first step from the previous acyloin condensation. the sodium is transferring a single electron, and after that, what is happening? if you have ethanol, then instead of the dimerization, it will move in this direction.





It will take the H^+ from the ethanol, it will form this compound with the carbon•. it will take one more electron from the sodium and form a minus here, which can take a proton from the ethanol. Now, you can see this carbon has a , OR and OH. So, you can clearly understand this will not stay here. It will immediately convert to the corresponding aldehyde.

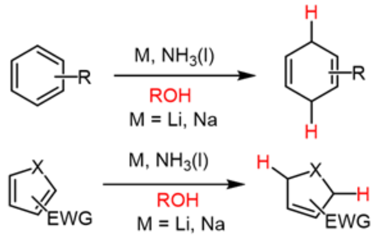
And now the aldehyde is going to get reduced with sodium. So, it is going to form the O^- and the C•. and then ethanol can give a H^+ to make the OH. you have a C•; now, the sodium can give one more electron to become a minus, and then once you have ethanol, it is going to form the corresponding alcohol. So, you can see here that if you have ethanol, then what is it stopping? It stops the first reaction, which is the second reaction of the acyloin condensation, which is the dimerization that is getting stopped.

So, you are getting protonated and getting further to convert to the aldehyde and then all the way to the corresponding alcohol. So, now we are going to move to a very important reaction in organic synthesis called Birch reduction. So, I am going to spend a lot of time here and try to understand and what are the different variations. So, this is a 1,4 reduction of the aromatic ring. So, this is a very important reaction because it reduces the aromatic ring.

So, this is a reducing aromatic ring, and you are forming some sort of a reduced benzene. what is happening? benzene is getting reduced. So, there is a 1, 4 reduction happening. Of course, depending on the R group there will be a selectivity difference.

we are going to come back to that discussion also. this reaction, first, we will try to understand the reduction of corresponding unconjugated cyclohexadiene and the heterocycle by alkali metals like lithium and sodium dissolved in liquid ammonia. So, we are taking this lithium, sodium, and potassium dissolved in the liquid ammonia, and we have an alcohol here, which is the source of the proton. In the presence of that, we can reduce the aromatic ring. it not only reduces phenyl but also reduces the corresponding heterocycle.

The 1,4-reduction of aromatic rings to the corresponding unconjugated cyclohexadienes and heterocycles by alkali metals (Li, Na, K) dissolved in liquid ammonia in the presence of an alcohol is called the **Birch reduction**.

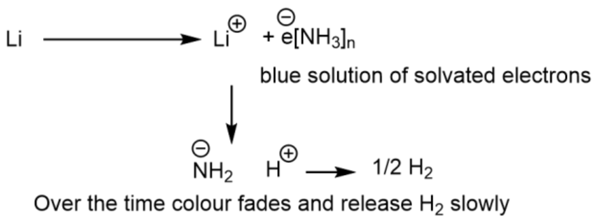


X = O, NR

- Reduction occurs at -33°C (boiling point of NH_3)
- many organic compounds are less soluble in NH_3, so Ether, THF or DME is used as co-solvent

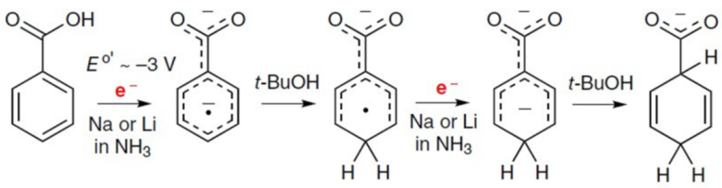
We are going to come back to the reaction. of course, the reduction occurs at -33 °C which is the boiling point of the liquid ammonia because you are using the reaction in the liquid ammonia. So, you have to do the reaction at -33 °C to continue the reduction happening . Of course, some of the time, the compound has a problem with the solubility in ammonia, so people can use the THF , ether in the reaction as a co-solvent with the ammonia. So, at the beginning of the reaction, in the sodium or lithium with the liquid ammonia, you will immediately see a blue solution of solvated electrons. So, if you are doing this reaction, the first thing is the formation of this blue color, which can indicate the solvated electrons are ready for the reaction.

Mechanism: (reducing agent)



Group 1 Metal	solubility in NH_3 (mol metal/mol NH_3)	Normal reduction potential at -50°C in NH_3(V)
Li	0.26	-2.99
Na	0.18	-2.59
K	0.21	-2.73

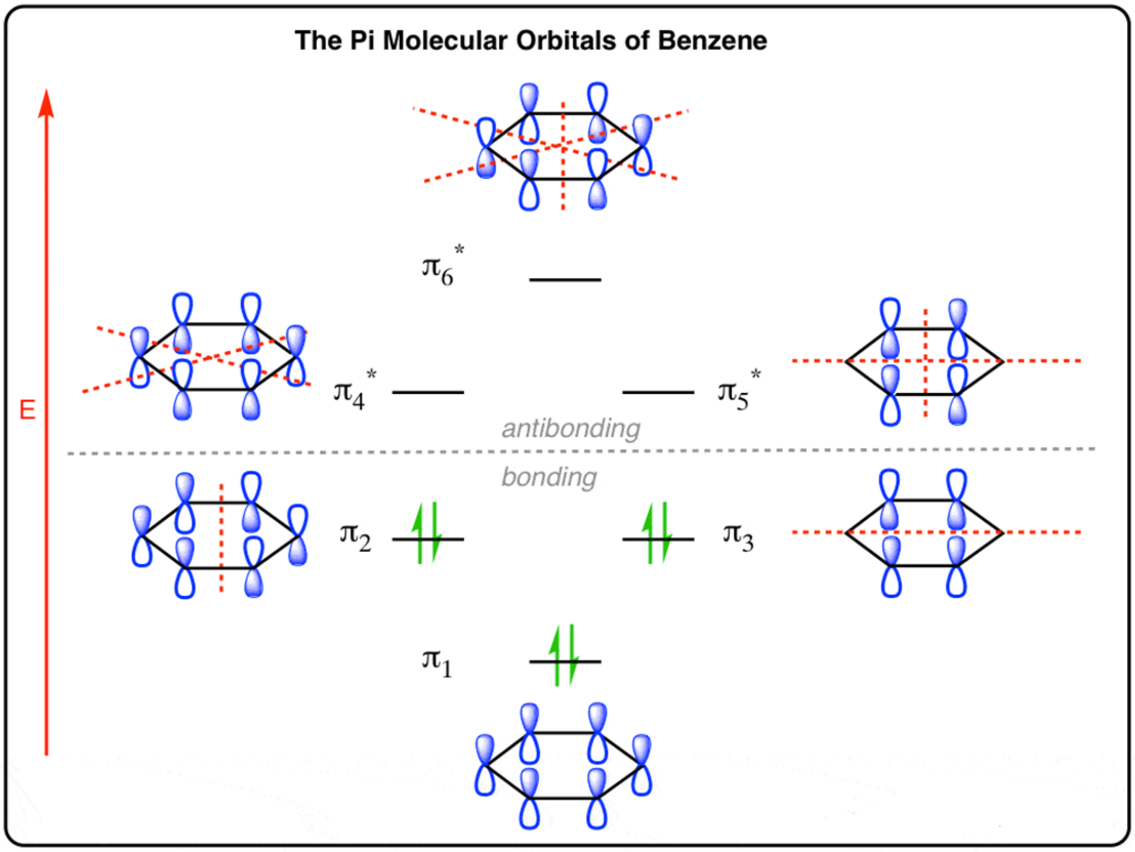
Benzene : -2.48V in MeCN



then you can add your substrate and continue the reaction. What happens? over time, the color fades, and it releases the H_2 slowly. That is why it is better that once you add the liquid ammonia and the sodium or the lithium, you also start doing your chemistry. Again, I think another important thing is that if you see the reduction potential. So this is very important because the reduction potential of benzene is 2.48 volt. So, you can see that if you have lithium with ammonia, then it can have a certain volt of 2.99. So, it can comfortably reduce the benzene. by sodium or potassium also. So, they can able to reduce the benzene ring ; we can clearly see from the reduction potential values.

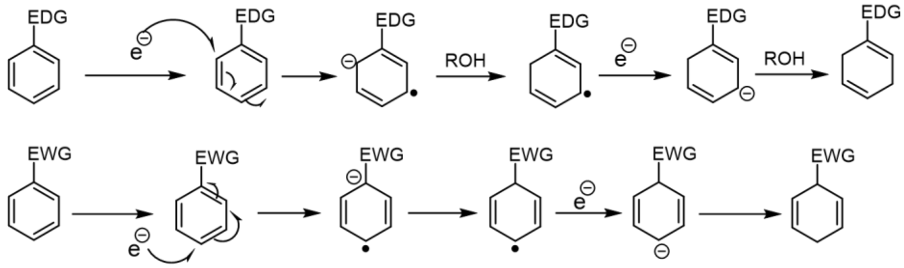
So, if you see the mechanism here, what type of reactions are happening and whatever functional groups you have attached here with the ring? Of course, we are going to come back to electron-donating group or electron-withdrawing group But first thing is what is happening? once you have this sodium and liquid ammonia you can see this solvent electrons will be transferred to the benzene ring. So, the ring will become something like this. you know lot of time you will see in the textbook. I am going to show the mechanism which is mostly given in the textbook. you will see the electron is adding in the particular position and forming a radical anion, but I feel it is better to write because if you see literally what is happening? the electron is getting to the ring and it is actually present everywhere in the ring.

So, it is actually a conjugated compound. So, you see the formation of a radical anion happening and that going to be take a proton from the tert-butanol here to form this radical species here. And now you can see there will be another electron going to be transferred from the sodium, going to form this anion and finally, you can see this anion will be forming next to this ester to get it stabilized anion. that is how it can take the proton from the tert-butanol to get to this corresponding product. So, if you see in this reaction, what is happening? where is this electron getting transferred? As I mentioned, for the carbonyl compound also, you will see the electron is getting transferred. what is happening? the single electron is going to the corresponding antibonding orbital.


The Pi Molecular Orbitals of Benzene

So, very similarly, in case of benzene also the electron is going to the corresponding antibonding orbital. So, that means, now you will have a 7 electron instead of 6 because now your electron will be in the antibonding orbital. So, that is how it is going to reduce the benzene As I mentioned that if you have a donating group versus electron-withdrawing group, electron donating group can stabilize the electron density in the ortho and meta position. So, if you have electron-donating group that can stabilize the electron density in the ortho, meta position.

Electron-donating groups stabilize the electron density of *ortho* and *meta* positions
Electron withdrawing group at *ipso* and *para* position



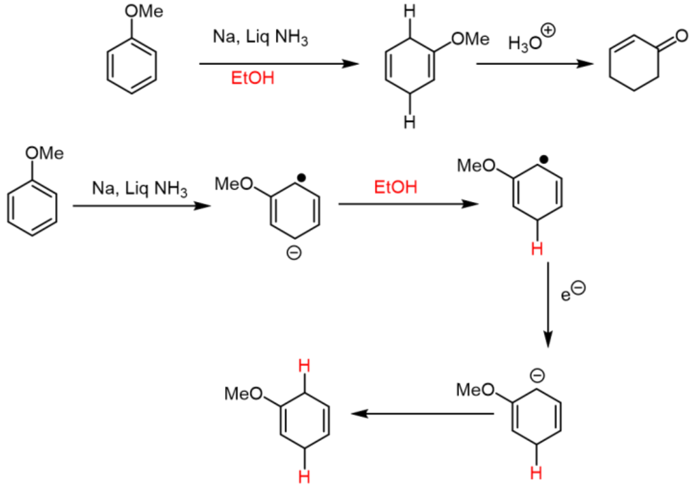
So, there will be ortho and meta selectivity. if you have an electron-withdrawing group, and then there will be a reduction happening in the ipso and para position. So that is the important thing. when you are trying to solve the problem on this topic then you have to understand that if you have an electron-withdrawing group then it is following the ipso and para position. if I have a electron-withdrawing group then you can clearly going to write that there will be product where hydrogen is going to be in this position.

Or you can say again both cases what is going to happen?. So, there will be ipso and para, but once you have an electron-donating group, this is going to happen. once you have donating group, after the reduction, you end up forming this compound. So, you see the hydrogen is coming in this position that is to the ortho and to the meta position. Now, we will try to understand how these things are happening. Of course, once you have an electron-donating group after the single electron transfer is happening, you are forming this minus and dot.

You can also write as a dot and a minus. these are, again, as I said, it is not that there is a minus here or dot here. It is actually a radical anion. So, that means you already have this electron transfer to the anti-bonding again. As I said, if you have an electron-donating group, that is going to stabilize the anion. So, it is going to get protonated here first, and then you can get one more electron from the sodium and is going to make anion here, which will take a proton and put an H here.

So, that is how you will see a reduction happening. Once you have electron-withdrawing group, once you give an electron, we have shown in the previous slide also that, radical anion formation is happening. Again you can see, you can write this as a dot minus (·−)or you can write a dot here and a minus here. but again once you form a minus it can take a proton from your ROH. So, there will be H here, then it can take another electron from the sodium and form a minus here, which can take another electron from the corresponding ROH to form the product.

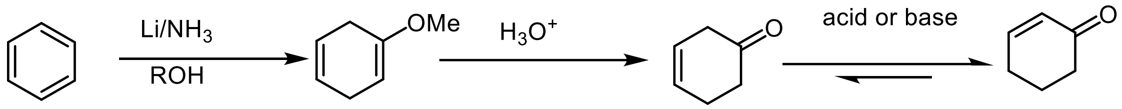
So, now you will see a formation of a ipso and and para selective product. So, again I hope you understood this part. So, let us try to solve some of the problems here. I think again if you have a methoxy we know there will be ortho, meta So, you will see this is the ortho position this is your meta position. So, there will be H on the ortho and meta position. of course, once you have a H_3O^+, what is going to happen? this is going to convert to the α,β-unsaturated carbonyl compound .

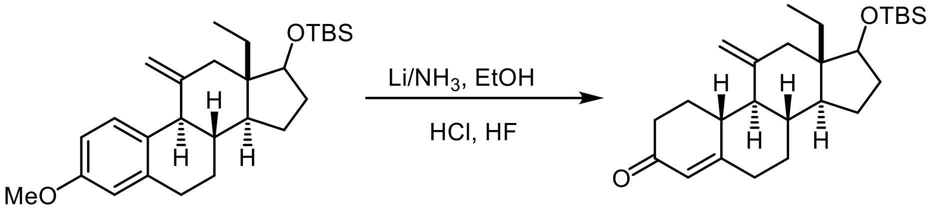

The **electron-donating** groups stabilize the electron density of **ortho** and **meta** positions

So, that, it is one very important thing that from this compound, you can easily able to convert to this compound in one pot manner. So, first do Birch reduction then treat with the acid, that will going to convert to this α,β- unsaturated carbonyl compounds. So, I think we have already discussed the mechanism. So, there will be a dot and the minus or sometimes you can write a minus here and a dot here also. I think either way, that is same as I said this is not the right things to write all the time.

It is actually a radical anion. We should write in that form where it will be delocalized in the entire ring. and then a proton addition, in this position or in this position, and then the next thing is another electron coming from sodium, and then again the protonation happening from the ethanol. So, here again this technique was used for the natural product synthesis. So, what is happening? if you see in the mechanistically, once you have a H_3O^+ it is going to form this compound, but in presence of acid and base what is going to happen? it is going to form the more stable compound. That is why it is going to get to this product, which is the α and β-unsaturated compounds, and then it can be applied for the natural product synthesis.

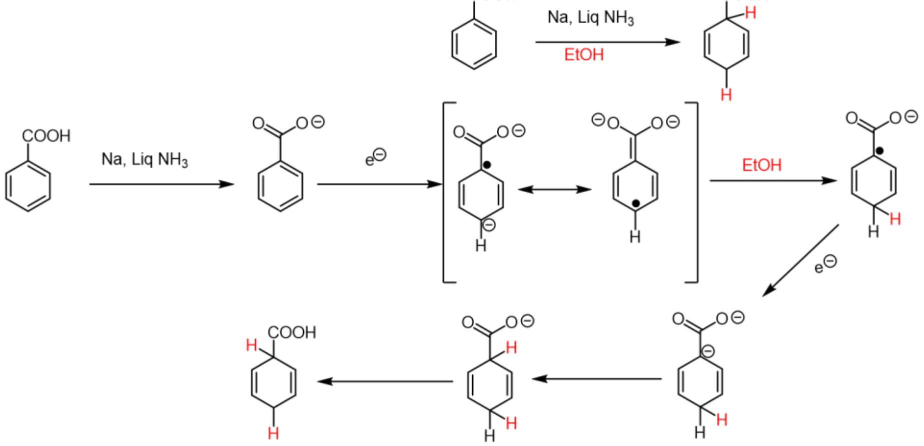
Another example here So, here you can see, you have this OMe group here in this ring. So, it is an electron-donating group, which means it is going to form this selectivity ortho, meta, but now once you have an HCl and HF in the reaction, that is going to convert to this to this α,β-unsaturated carbonyl compound.



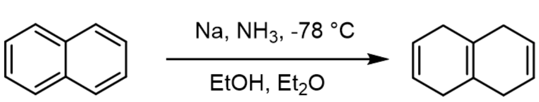


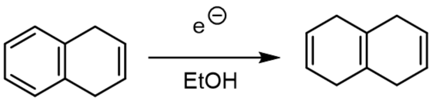
So, again, you have seen the effect of substitution in the Birch reduction; you have an acid, I already talked about that is going to go for this 1,4-reduction. So, that is going to be in the ipso and going to be in the para.

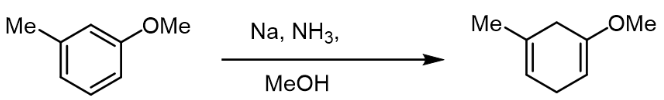
Electron density at **ipso** and **para** positions are stabilized by **electron-withdrawing groups** which result in the protonation at these positions.

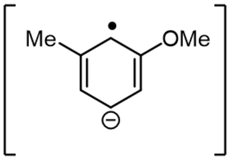


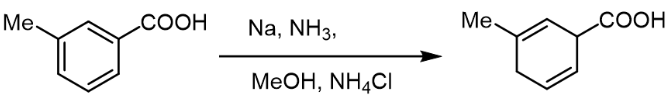
I think I already talked about the mechanism in the previous case. It followed a very similar mechanism which I have already discussed before. Here are some of the examples. here now we are talking about the naphthalene. Once you have a naphthalene, one of the ring is getting reduced to get to this compound here.

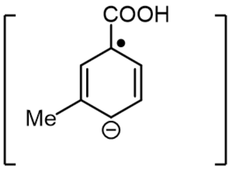










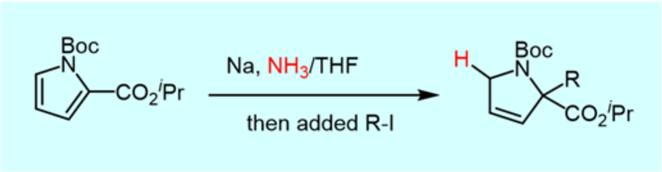


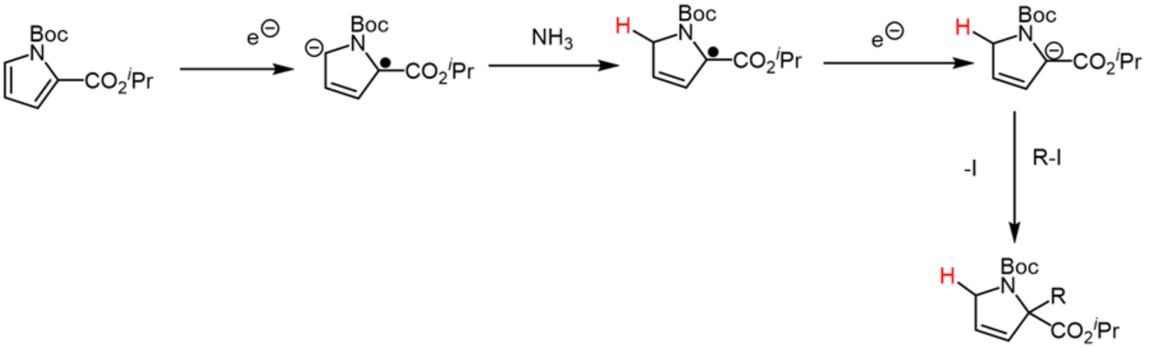
You can see this is very similar to the benzene ring. you can see, there is a H coming here. So, again this hydrogen is coming from the corresponding ethanol. Again you can see here, in this compound, you have a methyl and a methoxy. again, the methoxy is going to be the electron-donating group.

So, that is going to follow the same rule that you have learned. So, it will be the ortho and meta. So, in this position, the hydrogen is going to be attached. Again we have already explained that it is going to form the species formation like that and then protonation and then further reduction. And again if you have COOH and methyl, the COOH will be the electron-withdrawing group. So, that is going to dominate.

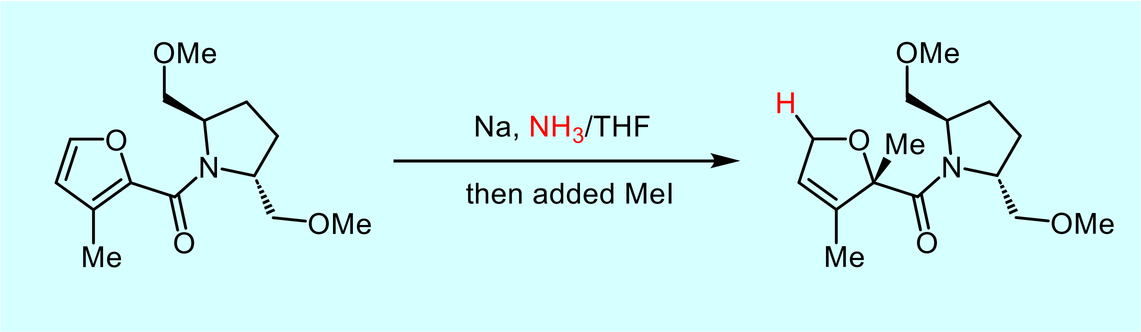
So, once it is going to dominate, you will going to form ipso and para. So, this position going to get proton. So, that is how you end up forming this product. Again we have shown that.

So, that is how, it is going to get reduced. here is another example of Birch reduction. So, here, in the Birch reduction instead of alcohol? If you have an alkyl iodide, what is going to happen? Of course, the first thing is once you have a sodium, it is going to give one electron to reduce the ring and going to form this radical anion species and now it is going to get a proton, and then once you have this radical here, that is going to take another electron from the sodium, to form a minus. Now you can see it is a stabilized anion, that is going to react with your corresponding alkyl iodide to form this quaternary center here. So, you have an R, esters, and there is carbon, and there is nitrogen here. So, that means if you have this scenario where you can add an alkyl iodide, then you can end up getting to the alkylation at the end.

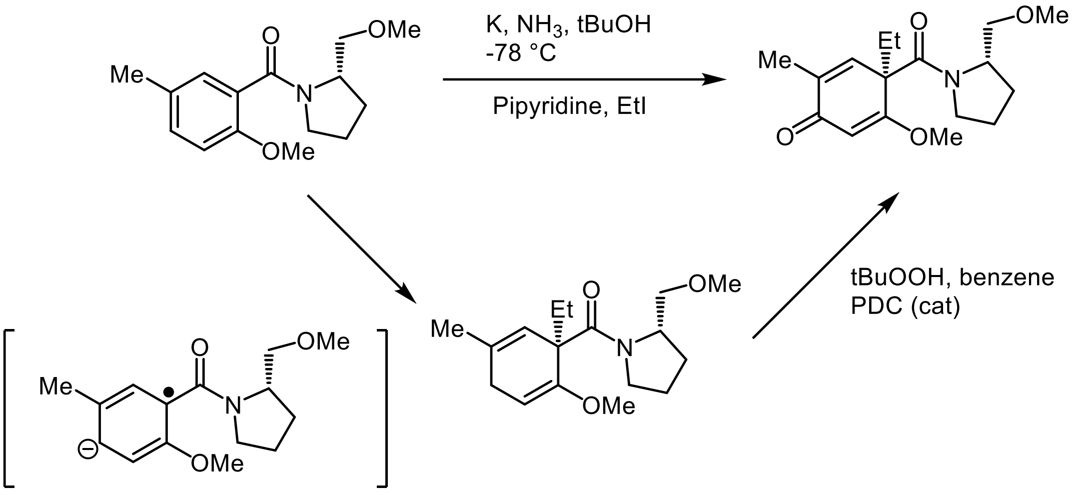




Another example here first thing is the reduction of this furan ring and then as you see there is electron withdrawing group on this side.

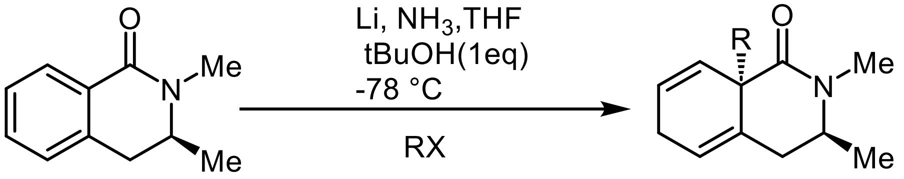


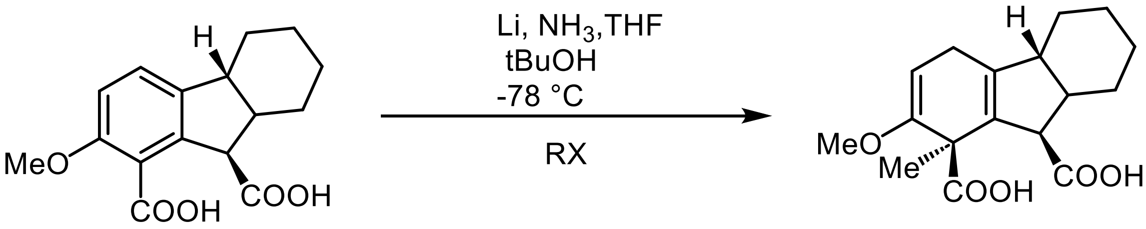
So, that means this radical anion will be stabilized, and that can be alkylated with the methyl iodide to introduce methyl group here. Another example here I think you can see, in this case, you have a OMe group, and you have this group here. you have an electron-withdrawing group. in the reaction what is happening if you have electron-withdrawing group here, then that is the one which is actually controlling the reaction that means there will be ipso and para position getting reduced. at the same time what is happening? there is an OMe going to be here. So, because you can see there is a ipso and the para position; there will be H here and there will be ethyl here that is going to act. So, now, if you have a PDC, which can oxidize this position. the allylic position getting oxidized to form the corresponding product. Another example of Birch reduction is here; you have the electron-withdrawing group.



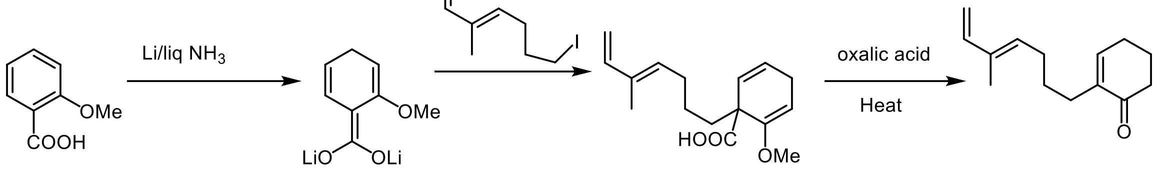
So, this is the ring, and you have an electron-withdrawing group, that, the amide group. you have liquid ammonia. You have the lithium, and the ammonia that is going to reduce it. So, then you have an RX, which means that it is going to go to the next to the ester. So, this is the carbon and there will be H here. So, the H and there will be R that is going to add again here in this ring you have a methoxy group you have a carboxylic acid group.

So, again, as I said, if you have a carboxylic acid group, then that is going to be the one going to dominate the reaction, and if you have alkyl iodide, you are going to add at the end, then what is going to happen? that is going to get alkylated here. So, there will be R here, if RX equal to methyl iodide; then you end up forming the methyl here, and there will be H here, which is coming from your alcohol here.



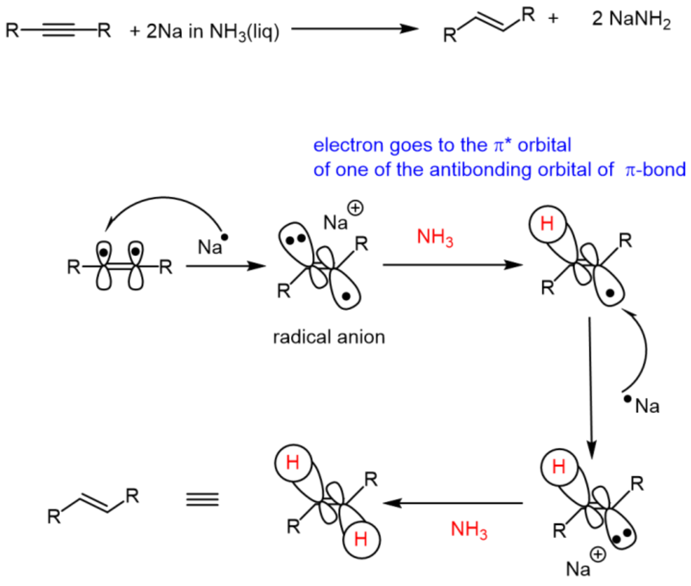


Another example here, so you have an acid, and you have an OMe group. I told you that in that case, what is going to happen? The acid is going to control it, it is going to form the stabilized anion, after the second step which can, with this alkyl iodide to form this compound. So, here what is happening at the end? There is an H, and this alkyl part is getting added in the ipso and in the para position; if you treat it with the acid, then it is going to form the more stable α,β-unsaturated carbonyl compound here.



Now, Here is the final part of Birch reduction. So, we talked about the Birch reduction of the aromatic ring. Now, we are talking about alkyne. So, the question comes if you want to reduce alkyne and form a trans olefin. I think this question is getting asked in the viva and also in the exam that if from alkyne, you want to get a cis, then use palladium, and then you use palladium in hydrogen, and you have to also use some poisonous catalyst.

So, that is why you have to use the Lindler catalyst. So, that can able to give you the corresponding cis because during hydrogenation with palladium, in presence of the palladium catalyst both the hydrogen approaching the same face. once you do Birch reduction, you end up forming the trans product. So, now question comes how this is happening here? Of course, in single electron transfer happening from the sodium to reduce the alkyne. So, there will be a dot, and there will be a minus here, and in that stage, then what is going to happen? there is a radical anion going to form at the beginning then there will be another sodium going to give one more electron.



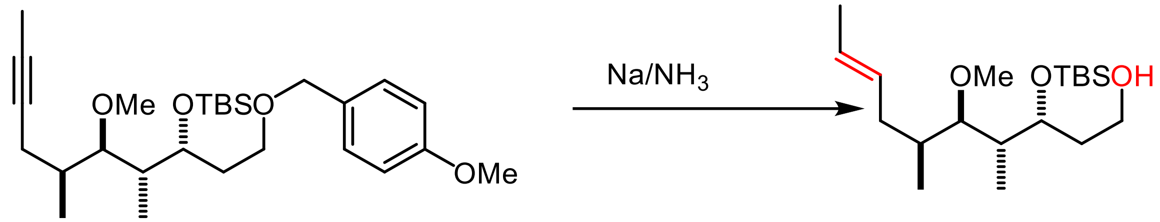
Although we don't generally think of NH_3 as an acid (**pK_a 38**), it is in fact a stronger acid than an **alkene C-H** (**pK_a about 42**).vinyl anion is basic enough to deprotonate NH_3

Vinyl radical is geometrically unstable and Choses to be ***E,***
Z-form has electron repulsion;
Inversion is difficult

So, now you can see the vinyl radical is geometrically unstable and chooses to be in E. The Z form has electron repulsion. So, what is happening? Once you have a radical anion formation happening, and then you have a protonation happening here, and then you give another electron. So, you have this scenario here. you have the electron density here. So, now, this vinyl radical formation is happening in this particular reaction, this we have a electron density one side. You have a vinyl radical. So, last if you come to this particular scenario. here, you give one electron first; what is going to happen? you have a vinyl radical in one side. you have an electron density. So, if they are in the Z confirmation they will be repel each other.

So, they do not want the repulsion. To stop the repulsion, they will arrange themselves in the E configuration. So, that is how the reaction is going to continue. So, this is the step, where your geometry is decided. because once you are in this position now you have a protonation here.

This radical will get another reduced. you will get one more electron to get anion. and it is going to get H. So, that is how the two of the H is adding to the trans version not in the cis version to avoid the repulsion between this radical and this electron pair. Here is an example. here you can see this alkyne is getting reduced here to form this corresponding alkene. So, here in this part, I talked about the dissolving metal-reducing agent. You have learned some of the single electron reduction; I talked about the acyloin condensation, the Birch reduction reaction, and then, of course, the reduction for the alkyne to get to the corresponding trans olefin.



I think these are the books you can follow for this part, and again and I am going to see you guys in the next class. Thank you.