Introductory Organic Chemistry - II
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Lecture 11
EAS: Effect of Electron Donating Group

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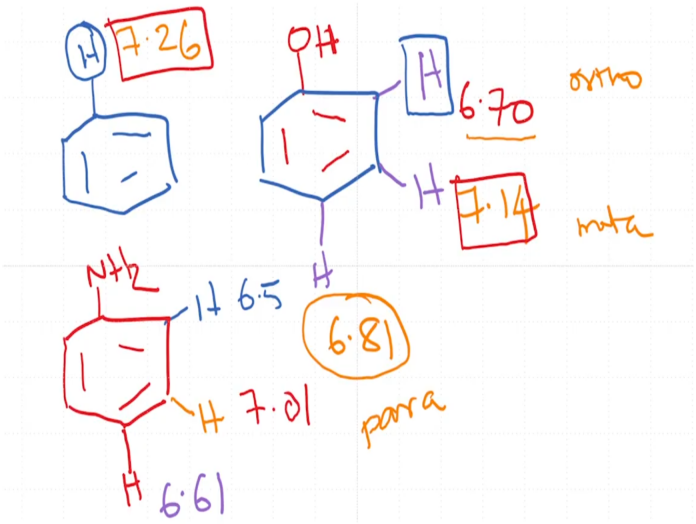

So, now let us look at some NMR data to try and understand the reactivity pattern in Phenol towards Electrophilic aromatic substitution. So, if you remember, the value for the chemical shift for Benzene was 7.26. And now in Phenol, what happens is that there is an asymmetry in the effect of the hydroxyl group. So, the ortho position for example, we have already sort of looked at previously that, there is in one of the resonance forms, there is a full negative charge in the ortho position. And so, you would expect that this position would have a lower chemical shift compared to Benzene.

And the important thing, let us move to the para position again, I mean before we go to the meta position. So, this is the ortho, these two, this is the meta, and this is the para. So, in the para position again we, if we recall there is a full negative charge in the resonance form or negative charge in the resonance form. And therefore, the para position, Hydrogen moved towards the lower chemical shift value. Now, in the case of meta, we found that there was no resonance form, wherein the negative charge spent was on this carbon or on this carbon.

So, therefore this chemical shift is very close to that of Benzene, 7.26. Of course, there is some effect because of the electron donating nature of the hydroxyl group through resonance but the effect is not significant. Now, when I look at this NMR spectrum, and when I compare it with another molecule of interest, which we are going to look at very soon, which is basically Aniline. We see a very, very similar pattern, NMR pattern. So, in Aniline, the ortho position, here the chemical shift value is 6.5.

And the meta position, as we would expect that there is no major effect, the meta position is 7.01, and lastly the para position is 6.61. So, if you look at these numbers and compare it with that of Phenol, the effect of the Aniline which is an electron donating group is very similar.

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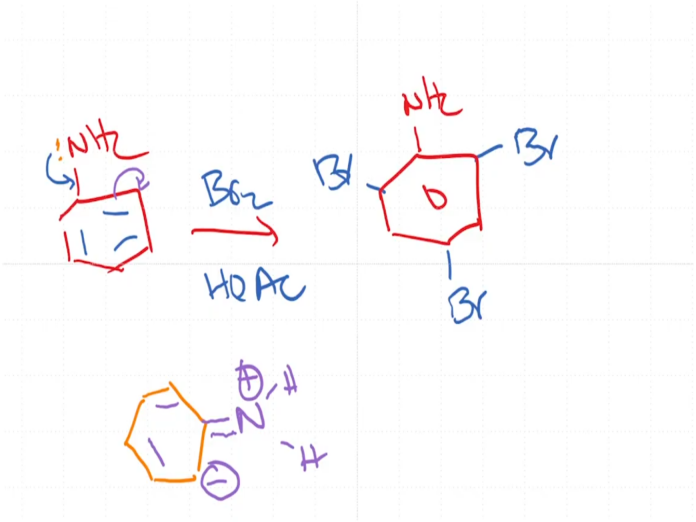

And as expected when you react Aniline with Bromine, you end up with the same sort of product where NH2, Br, Br and Br. So, you get that triBromoaniline as the major product. And typically, these reactions are done in bromine and acetic acid, so you do not need a Lewis acid to carry out this reaction.

So, just to sort of complete the discussion, you have an Aniline with a lone pair on the Nitrogen. And I am just going to draw a resonance form, wherein this goes to the ortho position and the

remaining part of the molecule is the same. So, just very much similar to Phenol. I think it will be a good exercise, if you go back and draw out the resonance forms.

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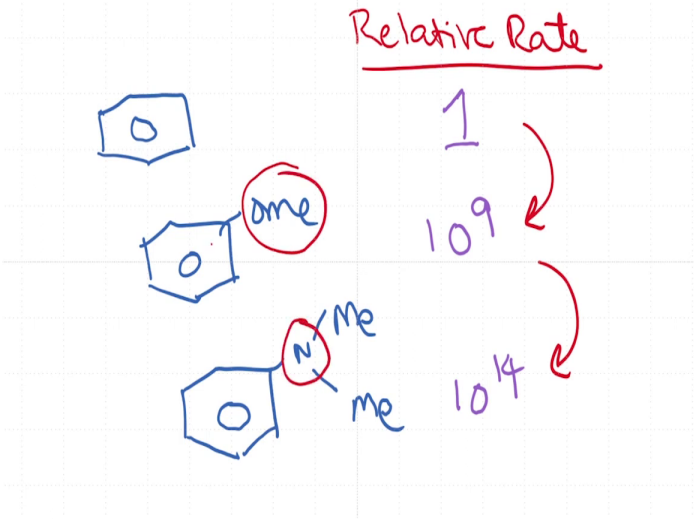

Now, let us understand the reaction rates. So, what I am going to do is, I am going to draw out some structures for you. So, what we are going to do is we are just going to compare the relative rates of bromination of these three compounds. And the way relative rate is calculated is that we measure the rate constant of the particular reaction of interest.

And then when we have a series, let say a, b and c and d, e and f, we take the lowest number and divide it by itself. So, then we would get a relative rate for example, Benzene is 1, and here this is 10^9, and this is 10^{14}.

So, there is a huge difference in moving from Benzene to Anisole, and a very large difference when moving from Anisole to N, N-Di-methylaniline. So, this is a very, very important concept for us to understand, that the electron donating ability of the methoxy group and the $N(Me)_2$ group is very strong.

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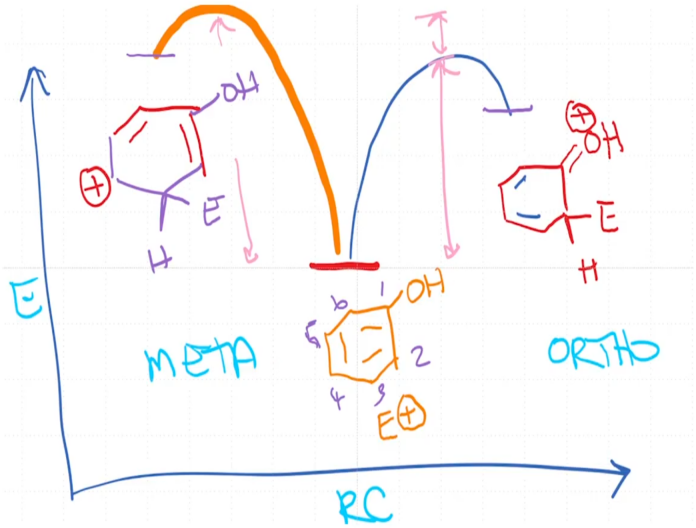

Now, what I am going to do is, I am going to spend a little bit of time and understand the energy profile of this reaction. Now, let us try and understand the reaction coordinate, so what we are going to do now first is to compare the energy profile of ortho versus meta. So, as we already know the major product in this reaction is actually the ortho and para products and the meta product is not formed. Even if it forms, it is really a minor product. So, from an energetic standpoint when we start out the energy of the electrophile and phenol must be the same, or this is the starting point.

Now, we know that the intermediate that is formed, when the substitution occurs at the ortho position is something like this. And then you can draw out multiple resonance forms which are going to give you the highly stabilized ortho intermediate. Now, subsequently the ortho intermediate collapses and gives you the final product.

What we also know is that, when you do a similar exercise for meta what you end up getting is a carbocation over here. Now, you can go back and try and push arrows as much as you want to, but you will find that there is no single structure where the hydroxyl group actually can interact through resonance directly with the positive charge. So, this becomes an impediment for the reaction of meta.

And so, if we were looking at the activation energy for this process versus the activation energy for this process, you will find that there is a substantial difference in this activation energy. And therefore, reactants predominantly go through the pathway of, going through ortho and para.

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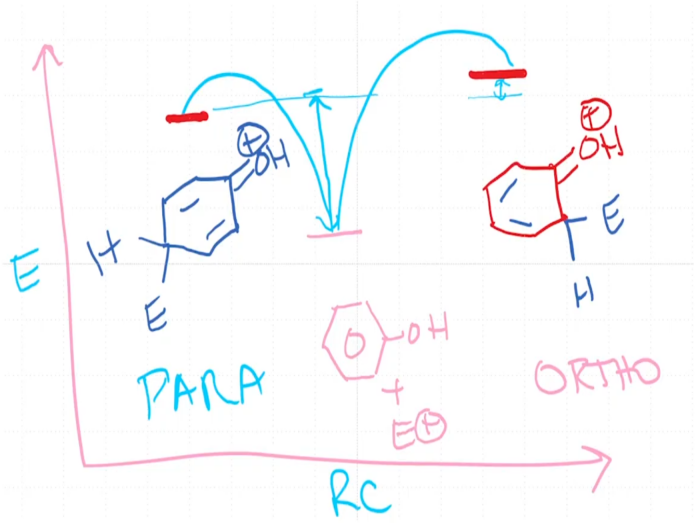

Now, to compare between ortho and para; we would like to locate this figure in the following manner. So, here is the same intermediate that we got with ortho, and here is the starting material which is E^+. And this is the same intermediate that we did, which we just discussed about the ortho product. Now, for para what happens is that you have an intermediate such as this, and what we know from our bromination reaction at lower temperature, which is in carbon disulphide, we know that the para product is actually formed preferentially over the ortho product.

And therefore, the barrier towards the formation of the para product, must be substantially lower than the barrier towards the formation of the ortho product. Otherwise, we would not be able to explain the product distribution.

So, in other words, the preferred product is the para product and the intermediate that is formed over here is stabilized substantially more than the intermediate that is formed here. So, one possible reason for this could be just sterics because you have the adjacent hydroxyl group that is

going to impede the reaction a little bit. And this is typically observed in ortho substitutions, where sterics play an important role.

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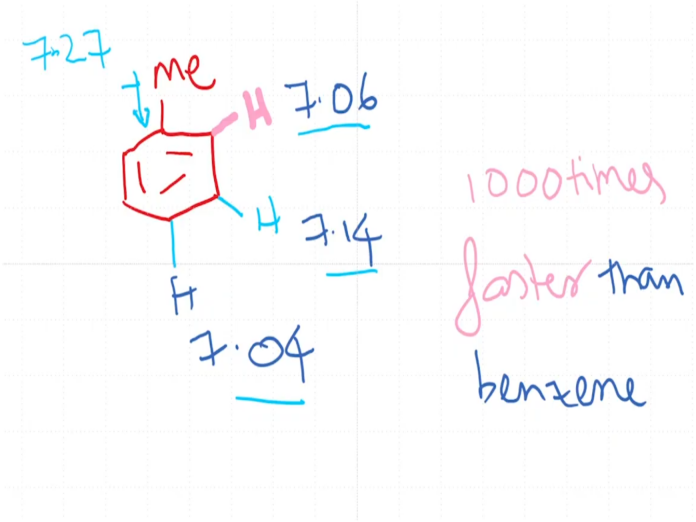

Now, we can now move on to other substituents. So, for example, when you look at Toluene, and if you want to react this with, let say you want to do a bromination on Toluene. The reaction occurs fairly well, we will look at the distribution but before that let us look at the NMR pattern. So, as you recall the NMR patterns of Benzene is 7.27 and so for Toluene, there is a shift towards lower chemical shift. And this can be explained by the electron donating inductive ability of this.

And again, as we discussed the inductive ability is somewhat stronger at the ortho position and the meta position. But nevertheless, it is not a substantial difference in inductive effect. However, when you look at the rate of reaction, this reacts 4000 times faster than Benzene. So, that is an important number because it certainly is not a small number but, so there is some stabilization afforded to the intermediate by the presence of the methyl group. Let us look at that now.

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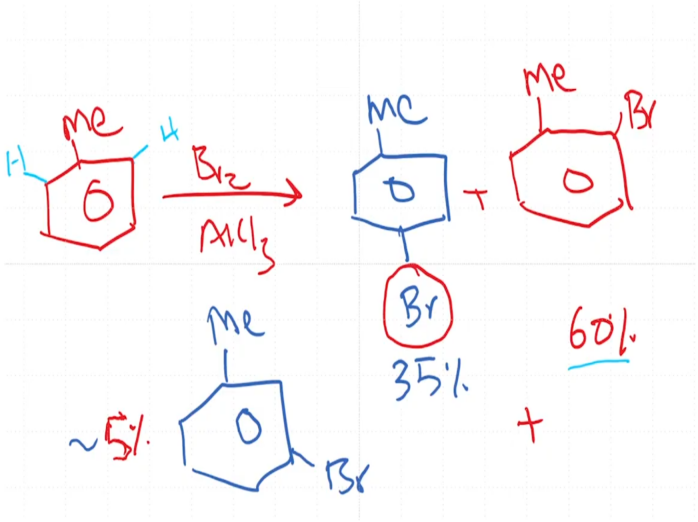

And now, we also will look at the reaction data. So, when you start with Toluene and react it, let's say we do a bromination. And you do need some Lewis acid for this reaction. So, when you do this reaction, you get about 35 percent of the para product. And then you get about 60 percent of the ortho product and the remaining is the meta product, which is a fairly no amount less than 5 percent or maybe around 5 percent. So, this observation, this result tells us that the preference for the para position is still higher here. Because statistically speaking you have only one para-Hydrogen that can be substituted, whereas you have two ortho Hydrogens that can be substituted.

So, therefore the preference, if I have to look at the reaction yields, so this is slightly less preferred compared to para. But we can also argue that it is comparable. Now, we want to understand why, I mean how this result or we want to explain this result.

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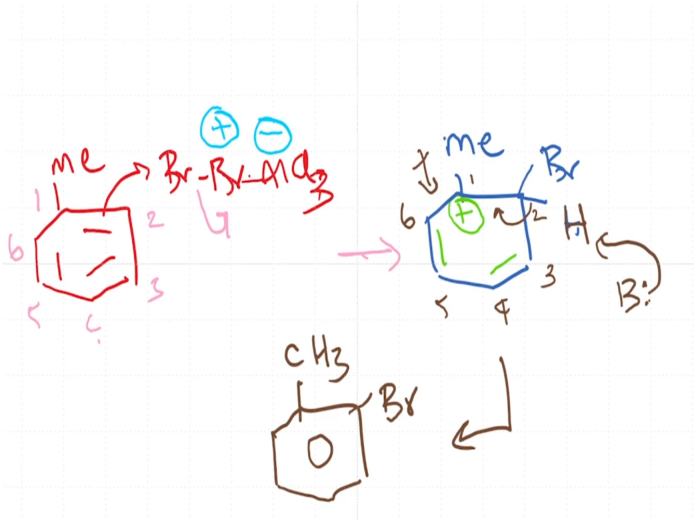

And the way we would explain it is again to go back, and look at the mechanism that we are now quite familiar with. So, Br-Br. Now, the only difference is you are going to do this in the presence of $AlCl_3$, so we write that out. And so, there is a positive charge here, and then there is a negative charge here. And you push electrons, you go here and the intermediate that is formed is, I am just going to draw it out for the ortho position and then we can discuss it for the other positions. So, therefore what is going on here is, if you see the number carbon 1, 2, 3, 4, 5 and 6, the bond between 1 and 2 is broken.

And so, you have a full positive charge, so it is going to be produced here. The rest of the molecule remains the same. And so here is the important structure in which the positive charge is actually a carbocation, which is now going to be stabilized by the inductive effect of the methyl group.

So, and of course the next step is the reaction with a base, which comes and picks up and then this moves here and gives you the ortho substituted Bromotoluene or 2-Bromotoluene. So, I will let you go back and work out the mechanism for the formation of the para product, which will again give you one resonance form where the reaction, the methyl directly interacts with the positive charge on the benzene ring.

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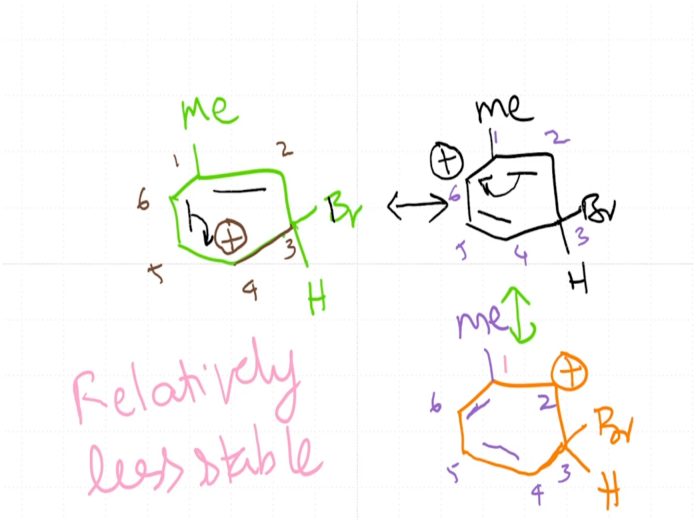

But now when you do the same exercise for the meta product, which we will quickly look at. So, what you going to get is, I have to number this 1, 2, 3, 4, 5 and 6. So we are breaking the bond between carbon 3 and carbon 4. So, you end up with the positive charge here, and this bond remains intact, and this bond remains intact. So, now If I have to draw a resonance form here, what we are going to get is Br here, H here and this is going to go over here, and there is the bond between 4 and 5 and there is a positive charge here.

And now we draw another resonance form here, and what we would get is, so the Br and H continue to be here. And you have a positive charge over here, and just to keep the same numbering 1, 2, 3, 4, 5 and 6, so the positive charge is on carbon-2. So, I am just going to number it here, 3 remains the same, 4, 5 there is a bond here, 6 your methyl group continues to be here, and there is a, this is carbon-1. So, this is going to be the, I mean the bond between carbon-1 and carbon-6. So, in none of these resonance forms, there is a situation where the methyl group directly interacts with the carbocation.

So, therefore these are relatively less stable when compared with the ortho or para forms. So, therefore one could explain the preference for the formation of the ortho and para in the case of Toluene. Although, the reactivity of Toluene is not as high as that of Phenol or Aniline because if you remember the relative rate for Phenol was 10^9. And the, and the relative rate for Aniline was

even higher. So, now to summarize this part, the electron donating groups either through induction or through resonance, typically end up with ortho or para substituted products.

And we understand this, because the preference for the reactivity at the ortho and para positions are higher and not only that the meta position is less stable. And therefore, the transition state leading to the formation of the meta product is going to be substantially higher in energy when compared to the other two. And when you are comparing ortho and para, sometimes statics come into play, but in general para is probably more reactive when you have groups that are going to interact by a resonance.