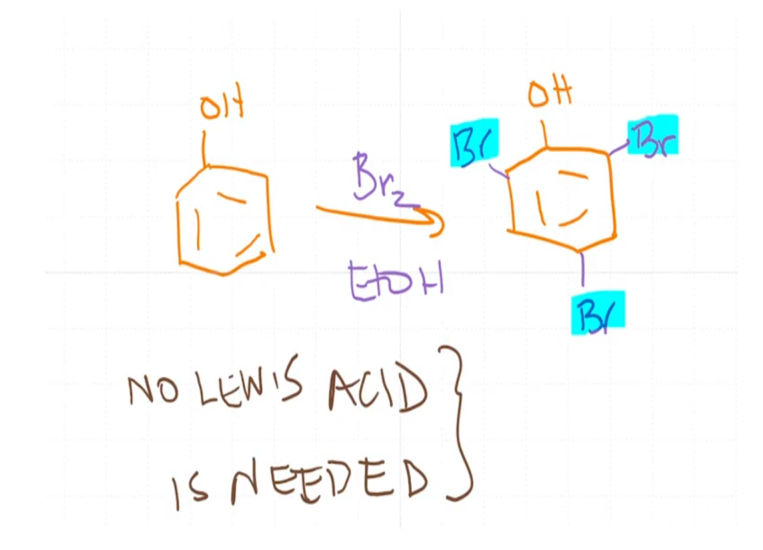


Introductory Organic Chemistry - II
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Lecture 10

Electrophilic Aromatic Substitution in Phenols

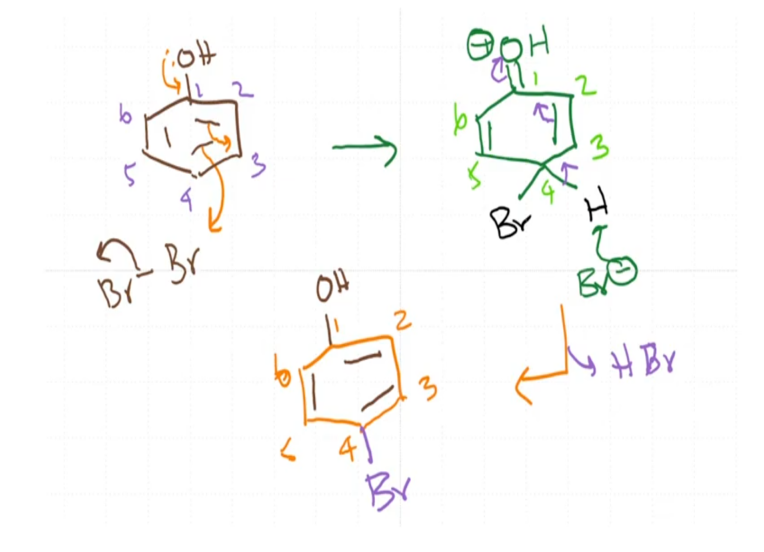
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So, in the lectures that we have discussed so far, we have primarily looked at Benzene. Now, we will start looking at substituted Benzenes. So, the first example that we are going to see is Phenol and this is going to be basically a bromination of Phenol. So, notice right away that this reaction produces not just one substitution, but actually it produces the tri-substituted product. So, you get three bromines in the product. The second thing that you notice is that there is no Lewis acid, so no Lewis acid is needed.

So, this is important because that means that Phenol is substantially more reactive when compared to benzene. So, you may recall that for bromination, we needed Br_2 and Aluminum Chloride. So, how do we understand these two results? The first one is that there is a bromination that is happening but it is happening only in three of the possible five positions and there are also multiple brominations. And the second result is that there is no Lewis acid needed, so they both are sort of related, and so we will discuss that now.

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So, let me just draw out an arrow pushing mechanism, and then we can sort of look at it in a little bit more detail. So, the first thing is that Phenol clearly is an electron donating group, although it is electron withdrawing by induction but it is electron donating by resonance. So, you can easily imagine that lone pair on Oxygen can be sort of given away. Let me just number these carbons, so that it is easy for us to follow. And so, what could happen is that you have Br and then you have Br, so it attacks here and bromide departs.

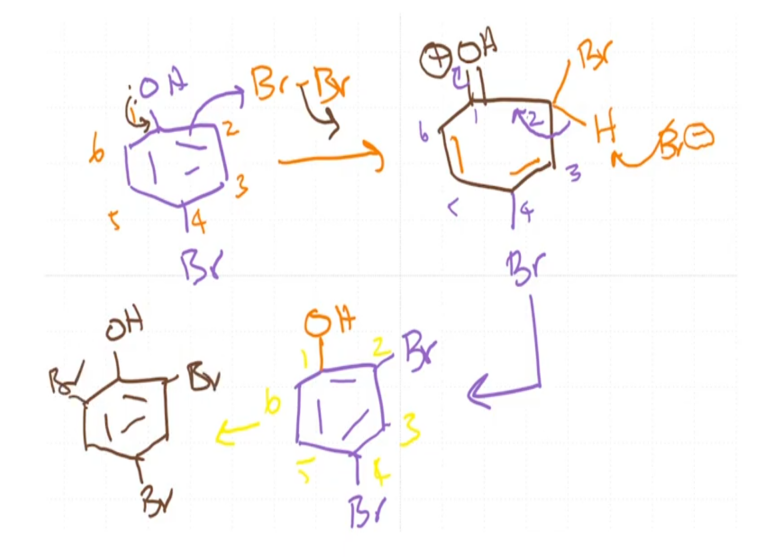
And therefore, the product that you would expect would be, so I am just going to keep the same 6-membered ring here. There is a bond between Oxygen and Carbon, so there will be O, H and that results in a positive charge here. There is no bond between carbon 2 and carbon 3; the bond between carbon 5 and carbon 6 remains the same. And carbon 4 which used to have only Hydrogen now also has Bromine. So, let me just do the numbering once again 1, 2, 3, 4, 5 and 6 and there is a full positive charge on Oxygen.

Now, you can propose that H^+ is being lost, and this could be taken up by Br^- for example. And there is a loss of H^+ and it happens in the following manner, so it can go back here and this can go back there, and this restores the neutral charge on Oxygen. So, let me sort of work this out step by step. So, first HBr is gone. So, let us write that out HBr and the second step is that in

carbon 4 there is Br, it still remains. And in carbon 3 and 4 there is now a double bond; carbon 5 and 6, the double bond remains. And there is a new bond that is formed here, and this is my OH.

So, let me number this 1, 2, 3, 4, 5 and 6, so this is how this reaction can occur and this sort of makes sense from many angles. One is that the OH group is quite electron donating through resonance and I do not see any problem in this mechanism the way it is written. Now, to understand the tri-substituted reaction.

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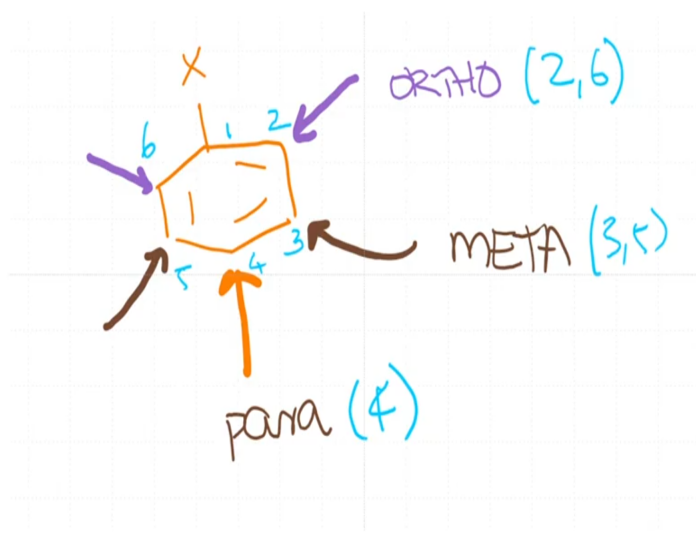
Let me just redraw Bromophenol, OH and Br. And so, you know you have an electron withdrawing group by induction, an electron donating group by, we will look at this in a little bit more detail. But the Phenol is still reactive enough. And so, it can sort of now react with another mole of Bromine, and this time it is going to attack in the following manner, and kick out Bromide. And we will stick to the same sort of numbering schedule 1, 2, 3, 4, 5 and 6. And so the product that is going to be formed, keep the same aromatic ring or benzene ring, and notice that you have the OH being involved because the OH is now involved by resonance.

And there is a new bond between this Carbon and Bromine and I am writing out the Carbon-Hydrogen bond, it is already there. And so, the bond between 1 and 2 is broken. So, 1, 2, 3, 4, 5 and 6, there is already a Br in carbon-4 and now the bond between 3 and 4 remains intact,

the bond between 5 and 6 remains intact. So, now if you have a Br⁻ or any other base attacking here, you can propose that this bond can break. And the new bond is formed, and it goes back to the Phenol. So, let us carefully redraw the structure, so Br is already here.

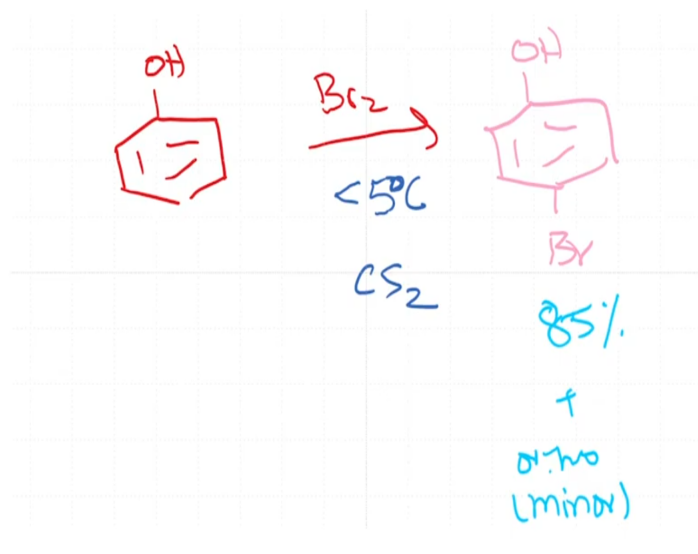
And now your OH is restored and just to complete the numbering this is 1, 2, 3, 4, 5 and 6. So, this is how the second Bromine adds and, I mean there is a substitution reaction. Now, I will let you work out the details of the addition of the third Bromine. And so, the final product that you get would be OH, Br, Br, and Br. So, now it is useful to sort of define these terms.

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So, when one draws a Benzene ring and it already has a substituent X. So, this position or these two positions are called as the ortho positions and this over here is called the para position. And lastly these two positions as shown here are called the meta position. So, therefore this ortho is basically, if I number the carbons, then the numbering would tell us how this happens. So, 1, 2, 3, 4, 5 and 6, see ortho is basically 2 and 6; meta is 3 and 5; and para is carbon number 4. So, in the case of bromination of Phenol we get the ortho and para substituted product, and you get the tri-substituted product.

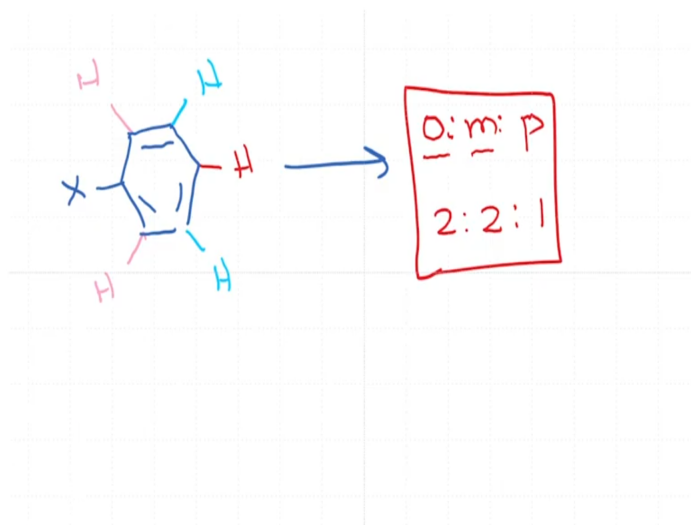
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Now, if you want to make the mono substituted product of Phenol, that is you just want to make one substituted Bromophenol. Then what you can do is, to reduce the temperature go to temperatures which are like less than 5°C and use solvents such as Carbon Disulphide and the product that you get is 4-Bromophenol. So, this also tells us that the para substitution is more likely to be the first reaction that happens because when you go to low temperature it is going to give you this as the major product, you also get the ortho product, but it is minor.

So, therefore if you want to make a mono substituted product, you may have to go to low temperatures in this case of compounds, which are highly reactive to electrophilic aromatic substitution. Now, we will spend some time and figure out why or how to understand this, this directing ability.

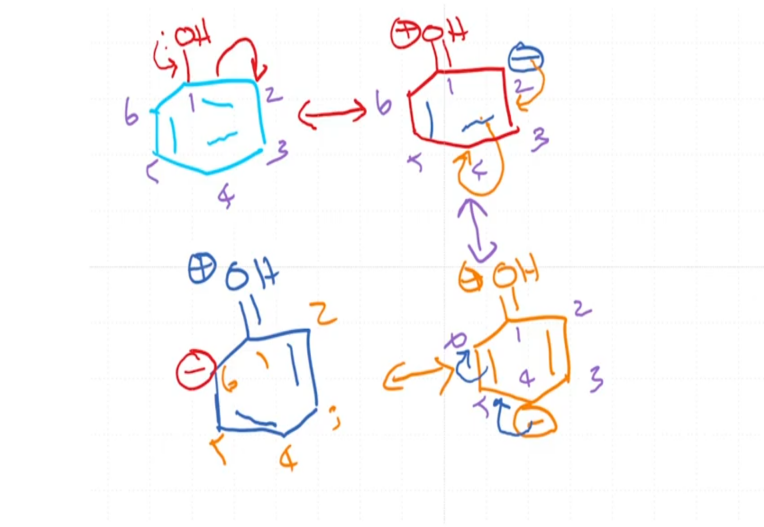
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So, what I mean by directing ability is basically, so when you have a substitution X here, and if the product that you get, if I just look at statistics then the ortho position as shown here has two hydrogens and therefore there are two substitutions that are possible. Also, meta has two substitutions, whereas para has only one substituent. So, therefore the ratio of ortho to meta to para purely by statistics should be 2: 2: 1.

And all your reactions if there is nothing else that determines the reaction outcome, the major two equally distributed products should be ortho and meta, and para should be the minor isomer. But in the case of phenol, you actually get para as the 85 percent yield product. So, clearly there is something else that is going on other than just statistics.

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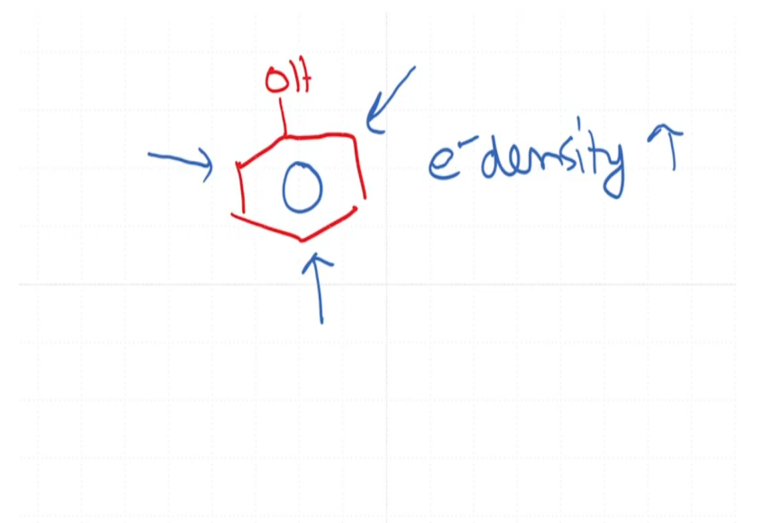


So, now we will try and understand what this process is. And now the way we understand it is let me again draw out Phenol. And so, this is the OH. Now, what I am going to do is I am going to draw some resonance forms. So, when I draw the resonance form of Phenol, so, I have OH, a positive charge here, and now there is a full negative charge over here, and over here. So, let me for ease of understanding let me just number these carbons, so, it is carbon 1, 2, 3, 4, 5 and 6.

So, if I have to draw the next resonance form, the way I would do this is to move this negative charge over here, and move this over here. So, this gives me the next resonance form where there is a double bond between carbon 2 and carbon 3 the rest of the molecule pretty much remains the same.

And lastly, if I have to get here, let me complete the numbering. So, lastly if I have to get the, one more resonance form is possible, so if I have to do that, I do it in the following way. So, the double bond OH plus remains the same, it is a bond between carbon 2 and carbon 3. There is a bond between carbon 4 and carbon 5, and now there is a full negative charge over here. So therefore, if you see the structures, the negative charge is localized in positions in the resonance forms in positions 2, 4, and 6.

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So, here with the Phenol, the negative charges are here, here and here and as per the resonance forms. So, it is not surprising that these positions are more reactive. So, the electron density on these carbons is higher. And this results in increased reactivity of these positions. We will also look at in more detail the energy profile at a later lecture. But this certainly contributes to the ortho, para directing ability of Phenol.