Introductory Organic Chemistry - II
Professor. Harinath Chakrapani and Dr. Neeraja Dashaputre
Indian Institute of Science Education and Research, Pune
Lecture 12
EAS: Effect of Electron Withdrawing Group

Now, let us try and understand what happens when we have an electron withdrawing group.

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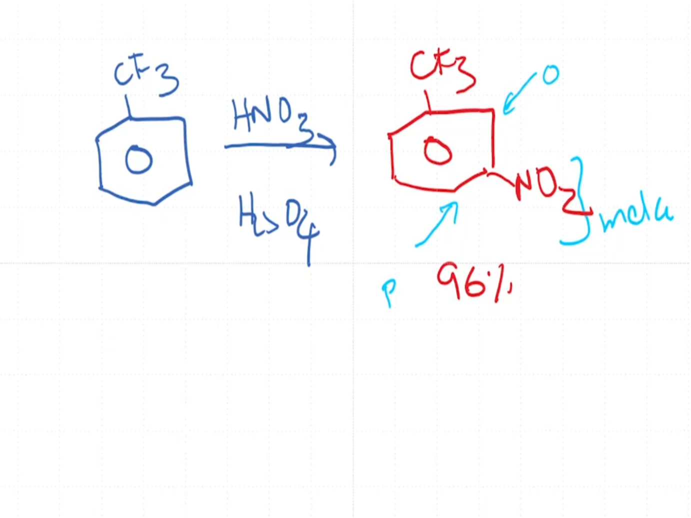

So, the example that we are going to look at is the CF3 group, so when we carry out a reaction and reaction that we are going to look at is nitration, $HNO_3 + H_2SO_4$. The product that is formed is $CF_3C_6H_4NO_2$ and the yield is 96 percent. So, this reaction works very well and gives you exclusively one product, which is the meta substituted product. So, this one is the meta, just to remind you this is the ortho, and this is the para. And also, this reaction is much slower than that of benzene. Now, let us try and understand this effect.

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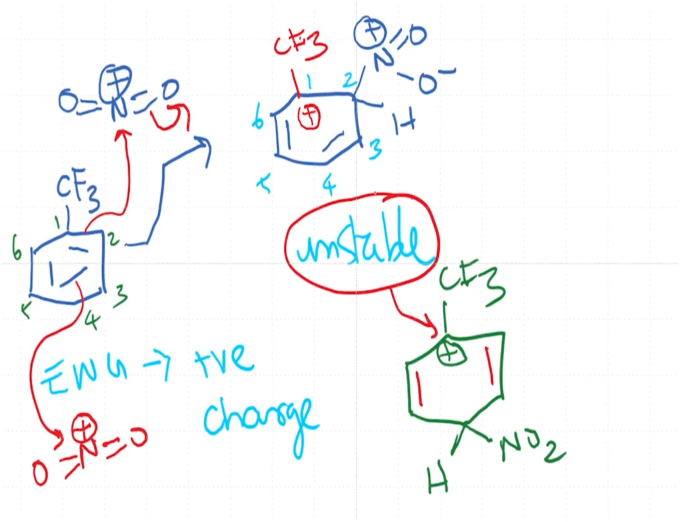

In order to understand this, we have to draw out some resonance forms, so let's just do that. So, CF3 as you know is an electron withdrawing group, so when it reacts with NO_2^+, so, let us carefully push electrons. So, this goes up here, and if I have to draw out the N double bond O double bond O, there is a positive charge. And then this goes here, so the product that is formed if it is in the ortho position is, N double bond O, O minus that is, it still has a positive charge, there is a hydrogen here.

And the CF3 group is here and there is going to be a full positive charge right next to this CF_3 group. So, what this ends up doing in this case is that you have an electron withdrawing group and the electron withdrawing group is right next to the positive charge.

And so, an electron withdrawing group next to a positive charge is not a good idea, so therefore one can expect that this would be quite unstable. Now, if we were to draw a sort of push arrows for this similar reaction with the para position, what we would end up getting is the formation of an intermediate, which is what I am just going to draw here. So, I would urge all of you to go back and do this on your own. So, what first happens is that you are going to have the bond between 3 and 4 is going to break.

But you can draw an additional resonance form, where the double bond between 1 and 2 moves and you get a full positive charge here, and with two double bonds here. So, again this structure is also unstable because it has a full positive charge next to CF_3.

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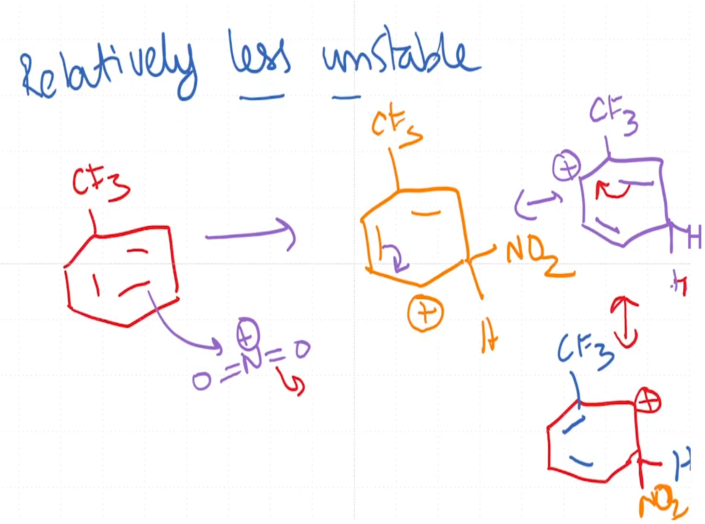

Now in comparison with this, let us now look at the meta position reacting. So, if you have CF_3 and again this is going to react with N double bond O, double bond O, plus charge. And this going out here, and the intermediate that we are going to have NO_2, H, CF3 and this bond is broken. So, you have a full positive charge over here and the rest of the molecule remains the same. Now, I draw another resonance form where we have this double bond moving over here. And you get a positive charge at this position and the rest of the molecule remains the same.

And now what you want to do is you can again do one more resonance form. And I am just going to draw it over here, where you still continue to have a positive charge. But, in none of these forms you have a situation where this NO_2 and this is hydrogen over here, in none of these cases you have the full positive charge right next to the CF_3 group. So, therefore we would call this as relatively less unstable.

So, the reason I am using two negatives here is because I do not think, I mean we are not suggesting that this compound is, this intermediate is very stable. Because it still has an electron withdrawing group attached to it. But when you compare this with the structure of ortho and para having an electron withdrawing group right next to the positive charge, creates a situation where it is going to be more unstable.

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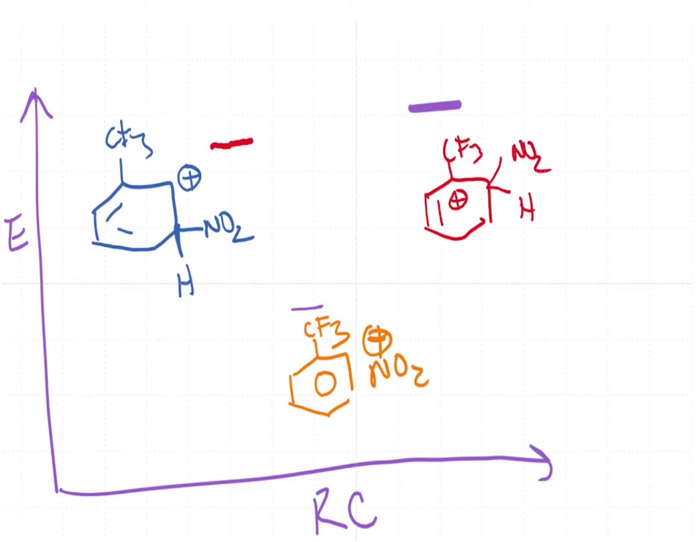

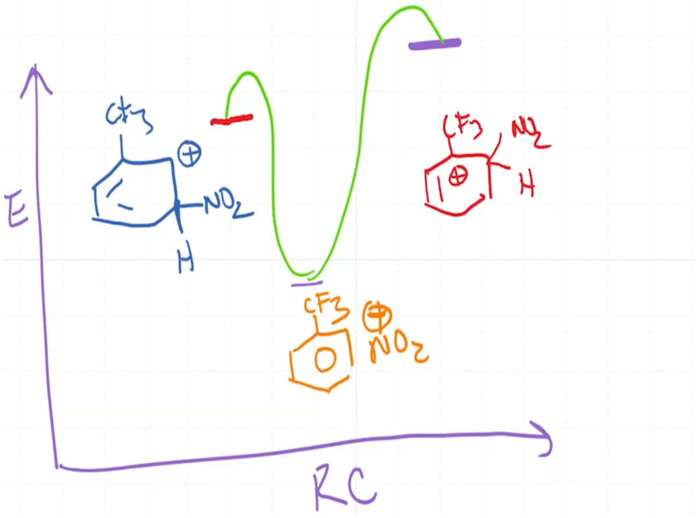

So, the preference for meta happens because or the way we understand it, is that the preference for meta happens, because the ortho and para are actually more unstable. So, if I have to draw out in the form of an energy diagram, let us take CF_3 over here, and then NO_2^+ as the electrophile. And if this reaction were to occur then let say that this is the intermediate that is formed with ortho. And this is going to be quite unstable, so there is no doubt about that. But, the one that is meta is actually going to be more unstable, so let say this is the ortho.

Now, the meta compound is going to have a structure, wherein the positive charge does not reside on the carbon next to the CF_3. So, therefore it is quite likely that the meta compound is going to be less unstable, which means that in terms of energy this is going to be a little bit lower than the ortho compound. So that is important, because once the ortho compound goes up in energy, then the rate of reaction for the ortho also substantially goes up. So, if this is going to be the energy profile here; for here, this is going to be the energy profile.

And of course, the next steps are the same, so it is basically the collapse of the intermediate. So, you can go back and draw a similar profile for comparing the meta and the para. But what we sort of conclude from this analysis is that the meta compound is actually, not like the meta compound is very stable. The reason it is formed is because it is less unstable compared to the ortho or para. You have a very similar sort of observation when you deal with the following compounds.

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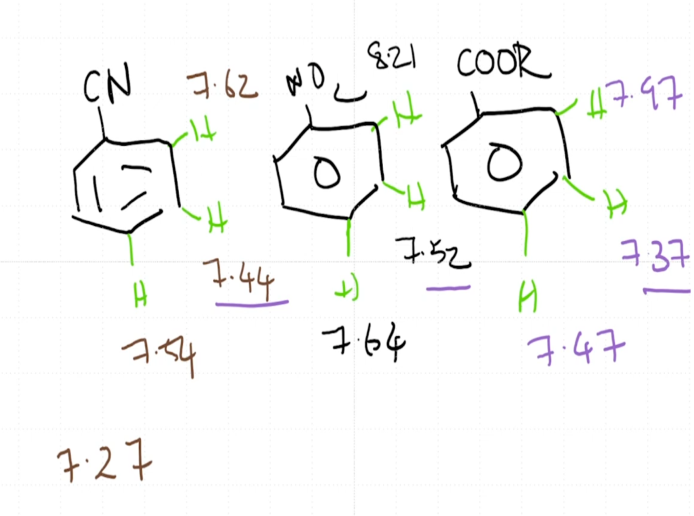

I am going to list it out and you can go back and look at it. So, cyano is a meta directing group, nitro is a meta directing group and you can also consider esters, aldehydes, ketones etc. All of them are a meta directing group, because they are all electron withdrawing. As a consequence, or as an inference we also see, that the NMR patterns of these compounds are very interesting. So, this is 7.62, this is 7.44, and this value is 7.54, keep in mind that the reference that we are looking at is benzene which is 7.27. Now, for nitrobenzene, similarly when we record the chemical shift values, the values that we get are 8.21, 7.52 and 7.64.

So, this is substantially moved, so if you look at the ortho position we have even moved from 7 to 8. And for the ester, we have the following arrangements. So, you have H, H and H. So, for ester we have the chemical shifts of 7.97, so it is fairly electron withdrawing. And as you see in the other cases also, meta position is not really perturbed as much as the ortho and para.

And so, they are all in the same range of, you know, be mere 0.1, 0.2 difference between benzene and them. So, all of these have larger chemical shifts when compared with benzene and the hydrogen in the meta position is least affected. And also, they are all meta directing, so when you do an electrophilic aromatic substitution on the molecules you are going to end up with the meta product.

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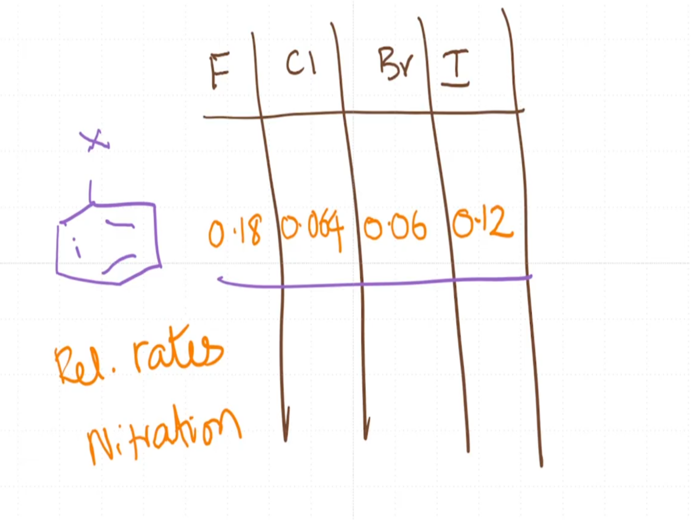

F	Cl	Br	I
0·18	0·064	0·06	0·12

Rel. rates
Nitration

The last set of compounds that we are going to look at, are actually very interesting. So, they are the halobenzenes. So, when we take X as a halogen, then the reaction rate is actually going to go down, so let us look at these numbers. So, when it is fluoro, chloro, bromo, iodo, these are the four compounds that we are going to consider.

And the first thing we are going to look at is the relative rate. So, the relative rate of fluoro is 0.18, for chloro is 0.064, for bromo 0.06, and for iodo 0.12. So, if you look at the relative rates of electrophilic aromatic substitution, what we are looking at is nitration. Relative rates of nitration, they are all slower when compared to benzene.

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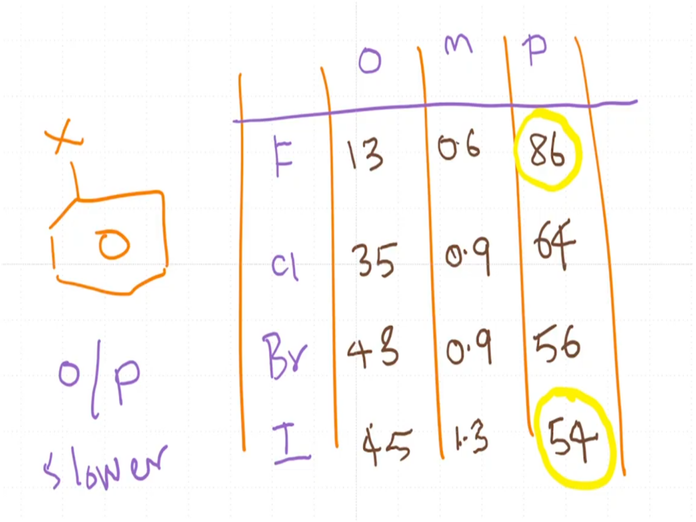

	o	m	p
F	13	0.6	86
Cl	35	0.9	64
Br	43	0.9	56
I	45	1.3	54

However, unlike the previous cases, when we look at the ratios, I am just going to draw it out again here. So, this is X, so I will list out. So, this is fluoro, chloro, bromo and iodo on the y-axis, on the x-axis what we are going to locate is ortho, meta, para. So, when we do this analysis what we find is that in the case of the fluoro, the ortho is 13, meta is 0.6, and the para is 86. So, 86 plus 13 is 99, so more than 99 percent you get ortho and para direction. The case of the chloro, this number is going up, the ortho goes up a little bit 35, then this is 64. But if you add the two of them it is still 99, and the meta compound is 0.9.

In the bromo, you have 43, again this is less than 1 percent and 56. And lastly in iodo, you have 45, the percentage of meta goes up a little bit to 1.3, and the percentage of para is 54. So, what we can conclude from this analysis is that it is a clearly ortho, para-directing group, but it is slower than benzene. Not just that, we also have this interesting observation that the percentage of the para substituent goes down, when we move from fluoro to iodo. So, which means that the ortho substituent starts to dominate. We may or we may not be able to completely understand these results, but we will make an attempt to develop a framework.

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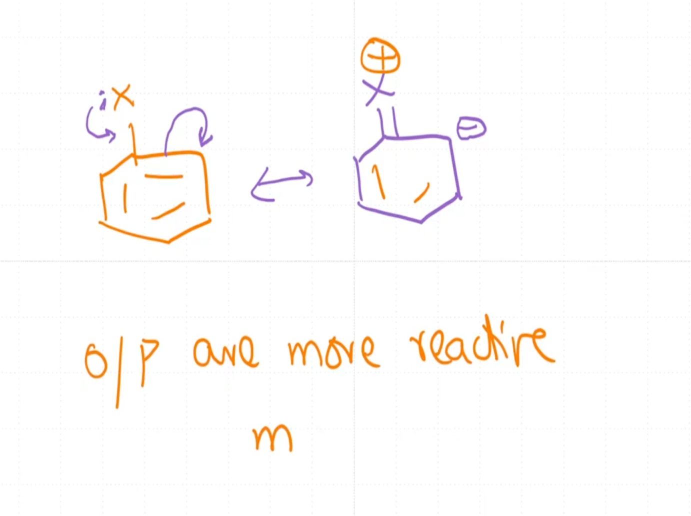

So, the first thing we need to look at is that, when we consider the halogens, we already discussed this. So, you have two types of effects; the first effect is a resonance effect, where you have a full negative charge that is going to be formed over here, in ortho and para position. And therefore, what we can expect is that the ortho and para are more reactive when compared with meta. So, this is something that we can use from previous discussions.

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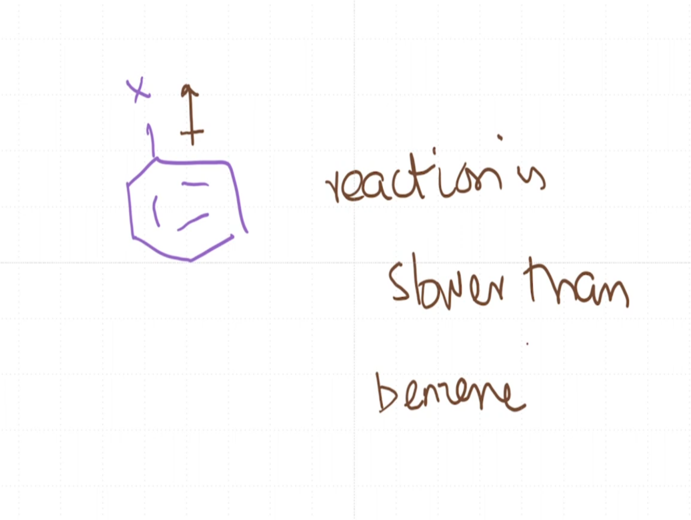

However, the problem with halogens, the situation with halogens is that they also have a strong inductive effect. So, they have a strong inductive effect which is going to pull electrons. So, this makes the reaction slower than benzene, because the electron density on the benzene ring is going to go down. But the intermediate that is going to be formed is going to be more stabilized, and the intermediate that we are going to be talking about is the one that is ortho and para.

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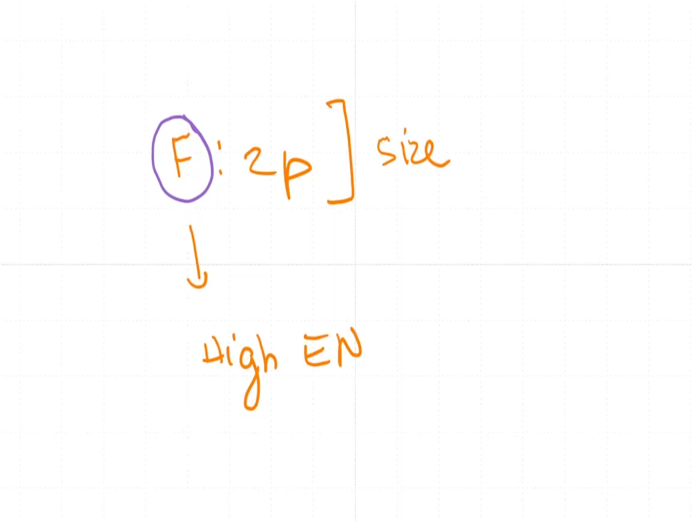

Now, among the halogens what we can sort of look at is that the fluorine is in the 2p orbital, and therefore it is a right, the perfect size, for it to interact with the benzene ring; carbon is also 2p. But the thing with fluorine is that it has a higher electronegativity, or the, one of the highest electronegativities. And therefore, the orbitals are much lower in energy. In the case of nitrogen and oxygen, electron withdrawing effect due to the electronegativity is not as important, but the conjugation is more important.

So, when we compare between or among fluorine, oxygen, and nitrogen, OMe and $N(Me)_2$ are substantially faster. We already look at the rate, it is really really fast. But, because fluorine, the electron withdrawing group effect, is important, the reaction rate is slower when compared to benzene. And when we look at the trend among iodo, chloro, bromo, and fluoro.

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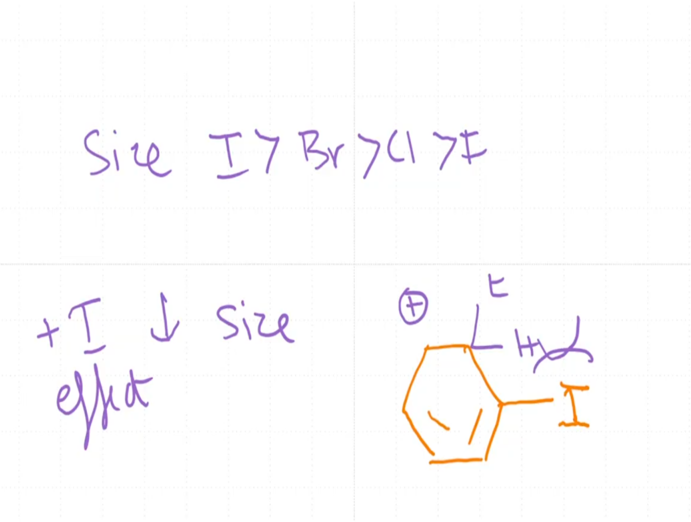
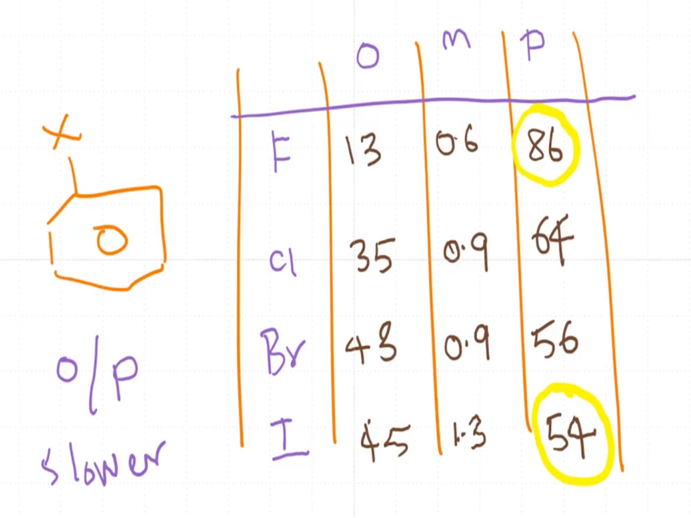


Size I > Br > Cl > F

+I effect ↓ size



	o	m	p
F	13	0.6	86
Cl	35	0.9	64
Br	43	0.9	56
I	45	1.3	54

So, the size of iodine is greater than bromine, which is greater than chlorine, which is greater than fluorine, so this is something that we have already looked at. So, the inductive effect decreases with size, so +I effect decreases with size. So, because of this the iodine is actually going to be a poorer inductive effect operating group. So, together what happens is that these two together are going to affect the reactivity of these compounds. Now, coming to the ortho and para sort of selectivity, so if I go back and look at this data, the ortho product is actually higher in the case of iodo.

So, one of the reasons for this could be the steric effect of the ortho positions. So, when we look at the iodo bond, so, what can happen is that the carbon-iodine bond is fairly long, and therefore the steric effect that one might expect to operate in the ortho position may not be as important. So, this repulsion may not be as important as what happens in the bromo or chloro. So, therefore the iodo compound has a higher proportion of ortho. Also keep in mind that the ortho substituent is, there are two substitutions, two positions that can be reacting. So, therefore statistically also, the ortho should be more favored compared to para.

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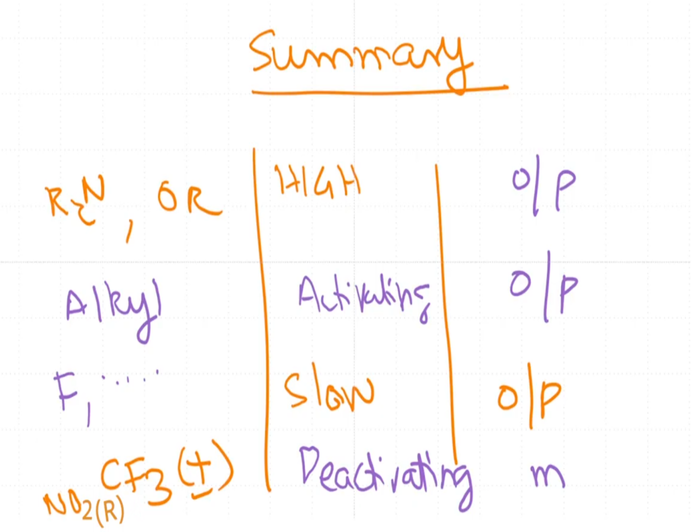

Summary

R_2N, OR	HIGH	o/p
Alkyl	Activating	o/p
F, ...	Slow	o/p
$NO_{2(R)}$ CF_3 (I)	Deactivating	m

So, to summarize, what we have discussed in these several lectures about directing ability. So, when you have NR_2 or OR, these are highly activating. Activating is really, really high. And they give you predominantly ortho and para products. Alkyl groups such as methyl, so they are activating and they give you ortho and para.

Now, the halogens F and Br etc. are deactivating, that is the reaction is slow, but they give you ortho and para. And lastly the electron withdrawing effects, so there are two types of electron-withdrawing effects; one is the CF_3, which is inductive and all the others which are nitro and cyano and so on, they are through resonance and these are deactivating and they give you the meta product.