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Deactivating Groups

Transcript

00:00:00:00 - 00:00:16:46
Dr.Jessie Key: We're going to switch gears now and talk about deactivating groups. Nitro is very electron withdrawing through both resonance and induction. Here are the resonance forms that we could draw for nitrobenzene.

00:00:16:46 - 00:00:33:44
Dr.Jessie Key: There are multiple resonance forms that we could draw. We can again walk our formal charge around the ring. Notice that formal charge is a formal positive charge this time and not a formal negative charge compared to when we're looking at the methoxy group.

00:00:33:44 - 00:01:05:30
Dr.Jessie Key: When we are moving our electrons around in our resonance forms here, notice that the electrons are coming up from the ring and giving us this formal positive charge on the ring instead of a formal negative charge. That's how we know it's electron withdrawing through resonance is that our resonance forms now have this formal positive charge here instead of a formal negative charge. Just to give you an idea of how deactivating the nitro group is, it will make the ring 100,000 times less reactive than benzene.

00:01:05:30 - 00:01:28:13
Dr.Jessie Key: Well, we're going to do the same thing that we did before with our activating groups and draw the sigma complexes that would arise when we put our nitro group on our ring and then try and perform a nitration. So here we have the sigma complexes that we will get when we have an ortho attack. With an ortho attack, we could draw these three sigma complexes.

00:01:28:13 - 00:02:04:23
Dr.Jessie Key: You'll notice that one of these sigma complexes here is highlighted in red, and that's because this is a particularly unstable resonance form. If you look at this resonance form here, highlighted in red, we have the formal positive charge located on the carbon directly attached to our nitro group. Placing this formal positive charge right on the carbon that's attached to a very electron withdrawing group is going to further withdraw electron density from this already electron deficient carbocation.

00:02:04:23 - 00:02:39:30
Dr.Jessie Key: This is a super unstable resonance form of the sigma complex having this nitro group here. If we went through the same exercise drawing out the sigma complexes that would arise from a meta attack, we would get these three resonance forms and none of them are particularly good or bad and that's why you don't see any of them highlighted here for you. With our para attack, we would get these three sigma complex resonance forms, and you can see in these three, we have two resonance forms that are not particularly good or bad.

00:02:39:30 - 00:03:14:50
Dr.Jessie Key: Then this one here that we have highlighted in red, again, is a very poor resonance form, and be very unstable because again, we have a formal positive charge located on the carbon with our nitro group. When we look at these three examples, ortho, meta and para, both the ortho and the para substitutions give us these intermediates which are incredibly unstable as one of the resonance forms. With deactivating groups, we tend not to see any ortho or para substitution.

00:03:14:50 - 00:03:31:67
Dr.Jessie Key: We pretty much only see meta substitution. Again, we can visualize this with free energy diagrams, free energy on the Y, reaction coordinate on the X. Here we have on the left here for an ortho substitution in the middle is meta and on the right is para.

00:03:31:67 - 00:04:13:54
Dr.Jessie Key: You can see that both the ortho and the para have very high activation energies and very high energy values for that sigma complex intermediate. Whereas the meta substitution, which didn't have any particularly good or bad resonance forms of the sigma complex, has this intermediate level of activation energy and this intermediate level of energy for our sigma complex. Almost none of it goes para and almost negligible amount going ortho, 93% going meta.

00:04:13:54 - 00:04:54:65
Dr.Jessie Key: Just to summarize what we've learned already, we see that electron donating groups are activating groups that will speed up our reaction and will direct the substitution to either the ortho or para locations and electron withdrawing groups are deactivating and will direct the reaction to occur at the meta position. Well, there is one weird exception to the rule and that is the halogens. Halogens are an exception because they themselves are electron withdrawing and deactivating, but end up giving us ortho and para substitution.

00:04:54:65 - 00:05:09:90
Dr.Jessie Key: The halogens are a weird exception to our general rules. Well, firstly, when you look at a halogen carbon bond, you would see that the halogens are electron withdrawing by induction. They would be deactivating.

00:05:09:90 - 00:05:30:99

Dr.Jessie Key: However, halogens donate electrons through resonance, just like we saw before with our methoxy group. Again, we can draw many resonance forms of our halobenzene. We can have those electrons come down and put a lone pair and formal negative charge, which we can walk around the ring just like we saw with methoxy.

00:05:30:99 - 00:06:02:24
Dr.Jessie Key: Halogens are a weird exception in that they can be slightly deactivating, but also still give us ortho, para substitution because of this resonance electron donation. We can take a look at the different sigma complexes that we would arrive at for our halobenzenes we would see that like before with the methoxy group, we have that additional resonance structure for the ortho and para substitutions.