Welcome dear students.

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Today we are going to deal with the topic from the paper CHC 103 Physical chemistry and organic chemistry.

The name of the module will be bromination and sulfonation of aniline.
The outline of the module will be discussion on electrophilic substitution in aryl amines and then we are going to understand bromination and sulfonation of aniline.

At the end of this module, you will be able to recall electrophilic substitution reactions, analyse the reactivity of arylamines in electrophilic substitution reaction. Understand bromination and sulfonation of aniline and then design synthetic scheme for particular desired product.

Let's start with electrophilic substitution in arylamines.

Arylamines means a compound where you have the amine group directly attached to an aryl group. The reactivity of the amine group and the aryl group are affected by each other. The electron delocalization reduces the basicity of amine.

As you can see in this example, where we are using aniline. There's a delocalization due to this unshared pair of electrons. Now the unshared pair of electrons on the nitrogen atom increases the electron density in the aromatic ring and makes arylamine extremely reactive towards electrophilic aromatic substitution.

As we already know that the lone pair of nitrogen will conjugate with the ring and thereby increase the electron density at ortho and para position of the ring.

Now because of this conjugation there will be resulting resonance structures and therefore we know that amines are called as ortho para directors, and they're also known as powerful activators. So, we see here that the incoming electrophile will be attached either at ortho position or at para position.

Coming to bromination of aniline. Bromination of aniline is one type of electrophilic substitution reaction, where the electrophile is Br^+.

Now when you take aniline and you react it with bromine water or bromine in acetic acid, you will immediately get a white precipitate that is of 2, 4, 6 tribromo aniline.

Now you see here multiple substitution, as bromine gets substituted at both this ortho and para position.

Now you get this product because NH_2 group is highly activating group. To solve the problem of multiple bromination we have to know how we get a monobromo derivative of aniline.

So, the strategy what we're going to use here is, we are going to protect then we are going to react and then deprotect. The first step to get mono Bromo derivative is to protect your amino group. Now this protection will decrease the activity of amino group by acylation with either acetyl chloride or acetic anhydride.

So, when aniline is reacted with an acetyl chloride or acetic anhydride, we see that there is an acylation happening here an your NH_2 group will get protected.

Now protection of Amino group is very important because the amide resonance within the acetal group competes with the delocalization of the nitrogen lone pair into the ring and hence this way it will moderate its reactivity. So, the lone pair is in competition, whether it should resonate with the ring or all along the acetyl group.

So here we see that the amido group is also acting as an activating group, but to a lesser extent then the amino group itself.

The next step after protection is your actual reaction. So, we react a protected amino group or the compound with bromine in acetic acid or you can also react with bromine water so you get two possible products either bromine substitution at para position or bromine substitution at ortho position.

Now we see here that para product is mostly the major product as due to steric hindrance of this group At ortho position this product will be in minor quantity.

The next step is deprotection, so once we react or once we perform bromination reaction, we have to remove the acetyl group which is protecting our amino group. Since it has served a purpose, it may be removed by hydrolysis and what you'll get is your amino group back. So, we see here that we can perform either base or acid hydrolysis and we can get our desired product.

I have written here one product because we have considered para product as the major product. So, if you have ortho product as well you'll get the corresponding product after hydrolysis.

So, to summarize this reaction, we know that this is the strategy what we have used, i.e., we have taken aniline and then we have protected it to give Acetanilide. Then we reacted this Acetanilide with bromine to give us para bromo acetanilide. So once the bromination is done, we have hydrolysed the amide to get para bromo aniline.

One thing what we have to note is that in case of benzene, when we're doing bromination or benzene,
We see that we use a Lewis acid that is FeBr3, but in this case we can't use this because your aniline can also act as a Lewis base, thereby giving this lone pairs on nitrogen to the lewis acid that is FeBr3 to form a salt so this will stop the reaction to move further.

Here I would like to mention that, we know that Lewis acid is also used in a Friedel crafts acylation reaction, So, Friedel crafts acylation reaction is not possible here.

Next, we move to sulfonation of aniline, sulfonation of aniline is also another electrophilic substitution reaction. We see here that when we take aniline and we try to sulfonate it, first we're going to get is anilinium hydrogen sulphate. Now when you heat it to 453 to 473 kelvins, there is going to be dehydration and also rearrangement to give you subsequent Sulfanilic acid. Now this sulfanilic acid can also exist as a zwitter ion. So, this is the general pathway on how this reaction proceeds. When this salt is formed

this acts as electron withdrawing group, it can also give you a meta product over here, but in minor quantity.

As you adjust the temperature, you are either going to get ortho product or you are going to get meta product as your major products.

To summarize this reaction, to get mono sulfonation product, what you have to do is you have to use the same strategy what we had used before. We'll take Aniline and then we are going to protect it, to give acetanilide, and then we're going to perform the sulfonation reaction. In the previous reaction we have seen that we have got multiple products that is ortho meta and para product a mixture of products.

So here what we're going to get is exclusively single product and then you deprotect it to give you sulfanilic acid.

To summarize, in this module we have recalled electrophilic substitution reaction. We have analysed the reactivity of arylamines in electrophilic substitution reaction. We have also discussed bromination, and sulfonation of aniline and we have learned how we can design synthetic scheme based on our desired product.

These are some references.

Thank you.