Introductory Organic Chemistry-II
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Lecture 7
Electrophilic Aromatic Substitution Part – 3

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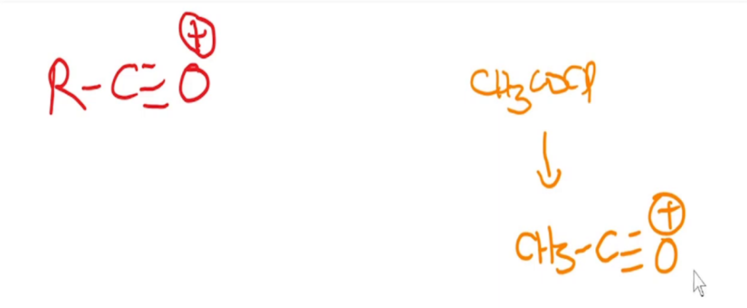

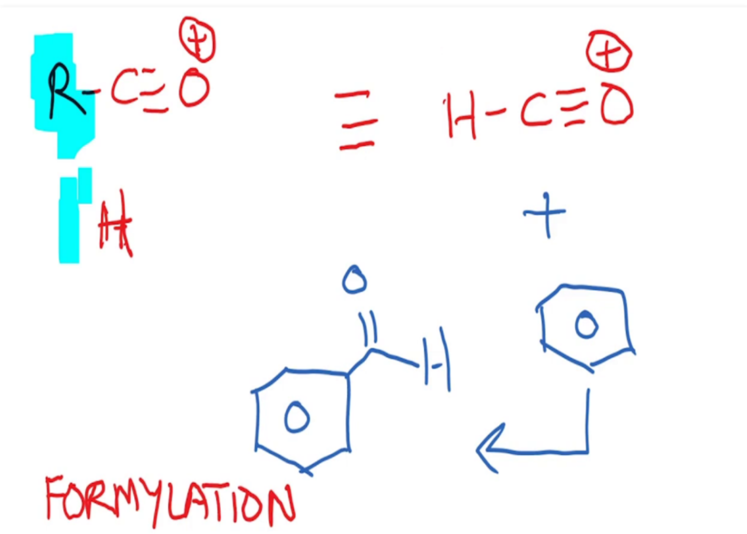

Now, let us move on. As we discussed, we know that the electrophile that is generated during the reaction is R-C≡O^{+}. So now, if we were to sort of, you know this R can be any alkyl group. So, if you start from acetyl chloride, you end up with CH_3CO^+, if you start with a longer chain carbon, you are going to end up with that corresponding product or the oxocarbenium ion.

So, now if we were to start with basically H, with R equals H, so if I replace this with Hydrogen. So, then we would get, you would want to generate an intermediate such as this, $HC\equiv O^+$ and this reacts with Benzene and then the product that you would eventually get would be, continues to be Friedel Crafts acylation except that you will get benzaldehyde. So, this reaction can be conducted, this reaction is known as a Formylation reaction. Just going to write it down so that you understand this. So, it is called a Formylation reaction and this Formylation reaction can actually be carried out under some conditions.

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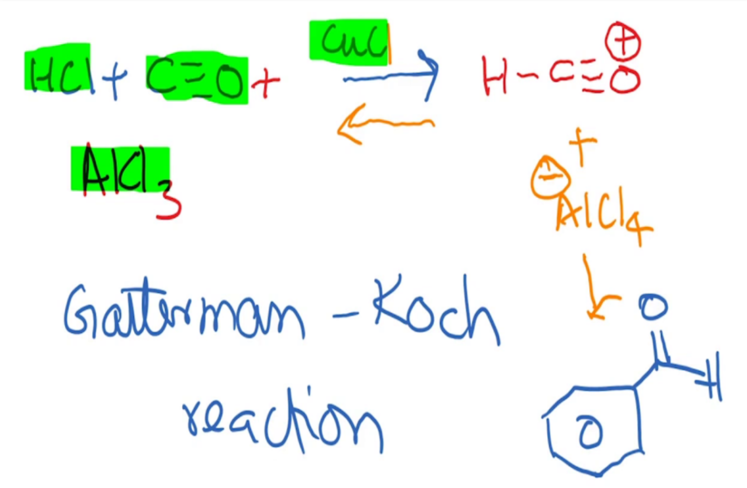

So, the conditions are as follows. Basically, we need to generate $HC\equiv O^+$ and this can be done by the following conditions which is reaction of HCl + CO, I think many of you know carbon monoxide and, plus a Lewis acid which is $AlCl_3$ and you also need CuCl and this is usually a reversible reaction. So, you will get $HC\equiv O^+$. and $AlCl_4^-$ which is a familiar reagent for us now and this, the conditions correspond to what is known as the Gatterman Koch reaction.

So, the Gatterman Koch reaction is nothing but the reaction of Benzene with these reagents as shown here, which is HCl, carbon monoxide, aluminum chloride in the presence of copper chloride and the product that is formed is actually the formylated benzene, which is the following, which is basically Benzaldehyde. So, the Gatterman Koch reaction is actually a modified Friedel Crafts reaction and it produces aldehydes on aromatic compounds.

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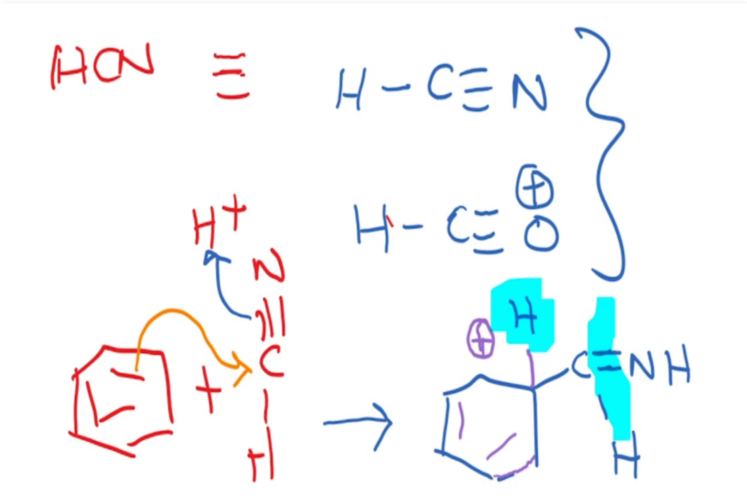

Now, there is a variation of this reaction, which is basically the, instead of using carbon monoxide, you could also use HCN, which is Hydrogen Cyanide. So, HCN is basically essentially HC≡N and if you recall the intermediate that we were looking at was $HC≡O^+$. So, if you see that these are actually isoelectronic and so, you can use HCN for this same Formylation reaction and reaction conditions that can be used are HCN in the presence of an acid and in the presence of, you can use HCl and a Lewis acid and it is going to give you the product.

So, the mechanism that we are looking at is basically the reaction of Benzene plus HC≡N and if you are doing this reaction in the presence of strong acid, then what can happen is, these attacks and this C≡N can break and it gives you the intermediate, and there is a Hydrogen that remains over here and you can generate a positive charge, as always in Electrophilic Aromatic substitution and this is the intermediate that is going to be formed.

And subsequent loss of proton, this can be lost and then you have hydrolysis around the C=N, it is going to give you the aldehyde. So, these are some modified conditions that can be used to generate aldehydes and even ketones for that matter and these are collectively known as the Gattermann reaction.

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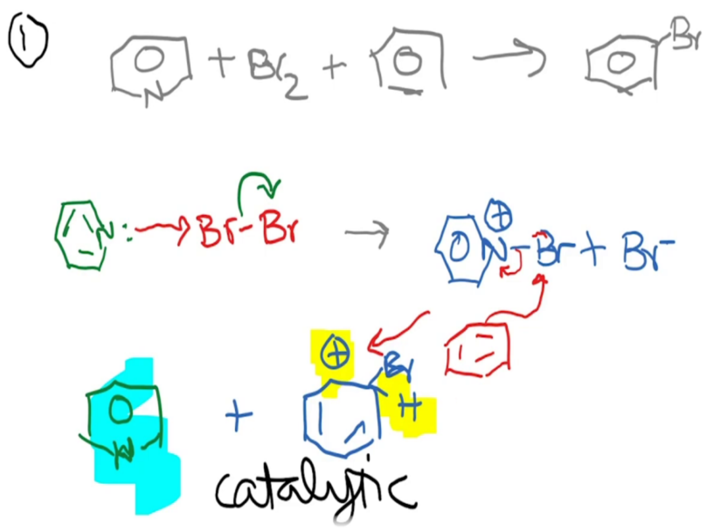

Now, let us discuss the couple of problems that we pulled in the class. So, this has been done, as I mentioned earlier, to make sure that you guys listen to the lectures. So, the first problem that we looked at was the reaction of Benzene in the presence of Br_2 really does not happen and if you add a small amount of Pyridine, it actually gives you the product which is Bromobenzene.

So, the question that we asked was what is the mechanism? How do you explain this observation? So, Pyridine, as you know, is actually a base. So, it is Aromatic, but the electrons that are present here, are actually quite basic, on the Nitrogen. And so, you can imagine that Br which is quite familiar to us that it is, Br_2 can actually heterolytically cleave to give Br^-, so you can think about a similar reaction where this attack and the attack actually produces the Br^- and Br^+.

So, the Br^+ is going to be in the form of a Pyridinium ion. So, your reaction is going to be in the following way. So, it is going to form N-Br and Pyridine actually acquires a positive charge, and it produces Br^- as a by-product. Now, this Pyridine complex, Brominated Pyridine complex, is actually quite reactive and so, you can imagine that Benzene is now, it is quite favorable for Benzene to react and give you a Pyridine as the by-product and give you the same complex that we normally are used to during Bromination.

So, it is going to give you Br, H and this is the product and it will give you Pyridine as the by-product. So, now as you can see, Pyridine becomes available for further reaction and therefore, it is actually catalytic and this complex can then further break down and give you the product, which is the Bromobenzene. Now, let us move on to the next problem, which is to do with the Friedel Crafts Acylation reaction.

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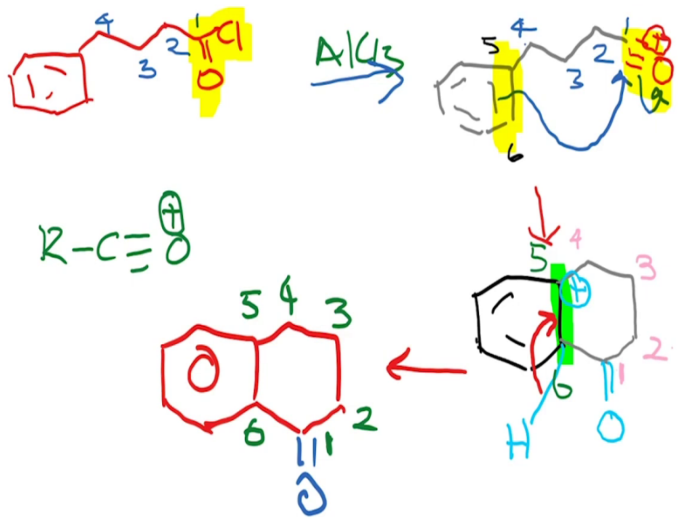

So here, the question that we had asked was the following compound, which is, what is the product that is formed when you expose this component to $AlCl_3$? So, I am just going to redraw the compound structure here and just to be clear let us number it, 1, 2, 3, 4 and so this was the compound and the question that has been asked is what is the product that is formed?

So, in order to address this question, let us look at what $AlCl_3$ could do in the presence of acid chloride. So normally, when we look at an acid chloride and aluminum chloride, we know that the following intermediate is going to be formed. So therefore, if you see, if you consider this scenario, so you are going to get, the Benzene ring would remain the way it is and then you have 1, 2, 3, 4 and if this is the carbon and acid chloride that is going to react and it is going to kick out chloro ion, then the product or the intermediate that you are going to get is $C{\equiv}O^+$.

Just to be sure, let us know just renumber this 1, 2, 3, 4 and then there is the benzene ring. So, numbering ways we are fine. So, this is going to be the intermediate that is formed. Now, what can this intermediate do? There are many things that the intermediate can do. One is there is some nucleophile present; it is going to react to that nucleophile and produce the product. But in this case, I do not see any other nucleophile being present here.

So, the other alternative is that it can do an intermolecular reaction and now this intermolecular reaction, of course, can happen and the intermolecular reaction could be the reaction of the benzene ring. But what is also possible is an intramolecular reaction and so the way in which the intramolecular reaction can occur is in the following way.

So, this is the electrophile, and it attacks on this Carbon and then you are going to have electrons being pushed over there. So, let us now draw out this product that we are going to look at. Now, what I will do is I am just going to number this so that it becomes easy for us to follow. So, this carbon that I am highlighting here, you can see that this bond over here is going to react and it is going to give you the product.

So, let me draw out the product as shown here. So, let us number this as number 5 and number 6. So, we redraw the Benzene ring and so there is going to be Carbon number 5 and then there is Carbon number 6, they are going to remain intact. And just to be clear, I am just going to highlight this over here and the rest of the molecule is going to be the same as far as the Benzene ring is concerned.

But now in this new ring, we have already determined that it is going to be a six membered ring and so in order to understand the six membered ring, we are going to see the numbering as we have done previously. So, this is going to be carbon 4, this is Carbon 3, this is Carbon 2 and this is Carbon number 1. And Carbon number 1 actually has the double bond O on it.

So, so far, we are doing fine. Now, we need to make sure that the product is written out correctly and so once this bond over here breaks, then you are going to form, there is going to be Hydrogen that remains here intact. So, this Hydrogen is going to be intact and there is going to be a positive charge over here.

So, this is going to be the structure that is going to be formed and now if we can propose that, there is going to be a loss of H^+ to restore aromaticity, then the likely product that would be formed would be the following. So, if you stick to the same sort of numbering; this is C=O and this is number 5, this is number 6, 4, 3, 2, 1.

So, this is likely the product that is going to be formed during this reaction. Now, I want you all to go back and look at the m/z ratio of this molecule and you should be able to get 146 as the m/z ratio that you would predict.