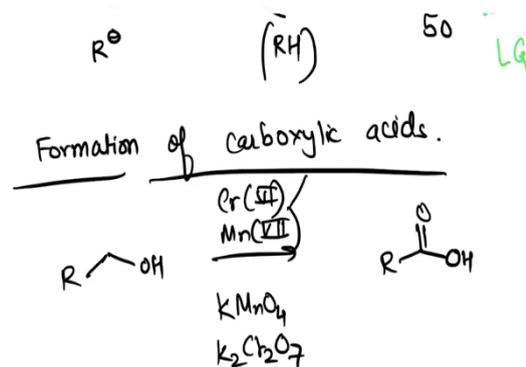


**Introductory Organic Chemistry- II**  
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**Lecture 28**

**Carboxylic acid and its derivatives - Part-2**

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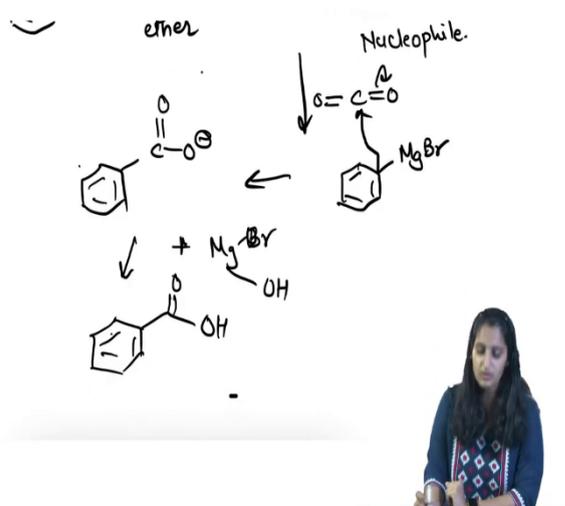
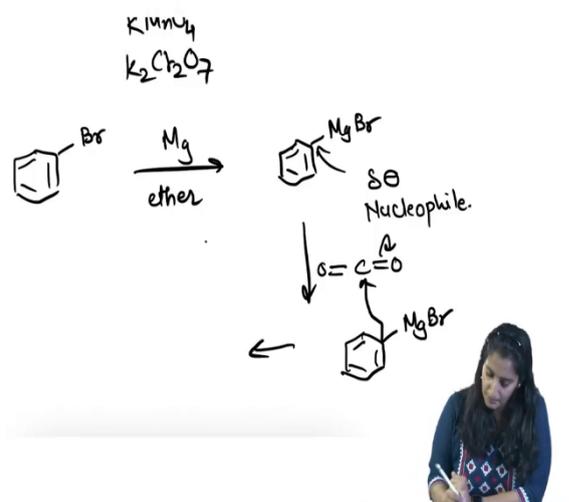


So, the other reaction that I wish to discuss in this chapter are somewhat either the reactions of carboxylic acids or their derivatives, some of the important reactions that we do or use in everyday life. We have one of the reactions is formation of carboxylic acids and these are the reactions that we have discussed a little bit.

One of the ways to form carboxylic acid is, of course, starting from primary alcohols. And you can take a primary alcohol like this, and then oxidize it all the way to a carboxylic acid. And typically, you have either chromium(VI) aqueous compounds or manganese(VII). Either one of these, to this or this and very typically reagents like  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ , all of these are going to play a very important role.

And I wish to discuss oxidation and reduction in much more detail later, so I will not go over this right now, but it is possible to oxidize it from alcohols to form carboxylic acids. Secondary alcohols will oxidize only up to ketones and will not form carboxylic acids at the end. And also, tertiary alcohols will not oxidize at all. So that is the reason.

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Now, let us go towards one more formation of carboxylic acid reactions, and this is with the help of a Grignard reagent. So, if I take for example, any alkyl halide or aryl halide, and if I treat it with magnesium in the presence of ether, this is under really dry conditions, we are going to form the corresponding Grignard. And this Grignard here, remember, the carbon here has a delta negative because it is more in the electronegativity as that of the magnesium. And what we are going to form is that this becomes our nucleophile.

Now, this particular nucleophile can react with a molecule like carbon dioxide. Now, carbon dioxide, remember, it is a gas, you are going to start with this, and you are going to attack it

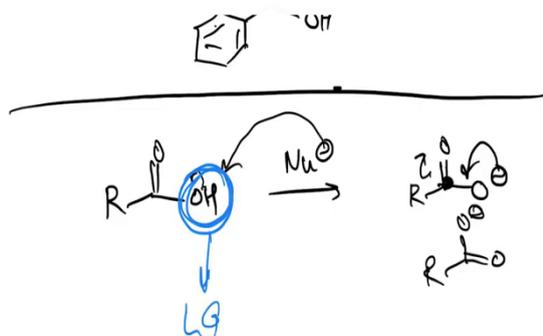
here, open this up. The true mechanism of this is a little different, but this is an easy way to do this particular reaction. So, what are we going to form here?

And when we put it in water, we are going to form the corresponding carboxylic acid.

So, the one way to form carboxylic acids is first forming the Grignard and then reacting with carbon dioxide. But remember that the carbon from the carbon dioxide is going to add on to the starting alkyl group that you have started with. And as a result of which you always have one carbon added to the end product.

These are the two reactions that I wanted to talk about while formation of a carboxylic acid, and later on we will look at the oxidization reaction or oxidizing agent's reactions in much more detail. The other reason why I wanted to talk about formation of carboxylic acids is, remember, that we have now seen how we can convert acid chlorides into various other functional groups or anhydrides into various other functional groups. What we have not seen is, how do we form acid chlorides or anhydrides? Well, the starting material for those is the starting acids.

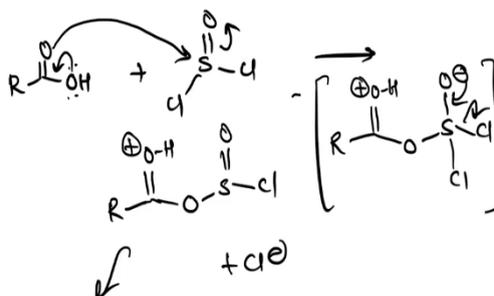
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And remember that acids themselves will not undergo this acyl substitution reaction very nicely, because as we were talking about most nucleophiles also good bases. So, let us say a hydroxide, a good nucleophile also a good base. What it is going to do is it is going to first deprotonate this and form the conjugate base. Now, this conjugate base has a resonance structure and thus this carbon has lost its electrophilicity towards the reaction. And thus, we

need to convert this OH into a much better leaving group. And that is where the chlorides and anhydrides come into picture.

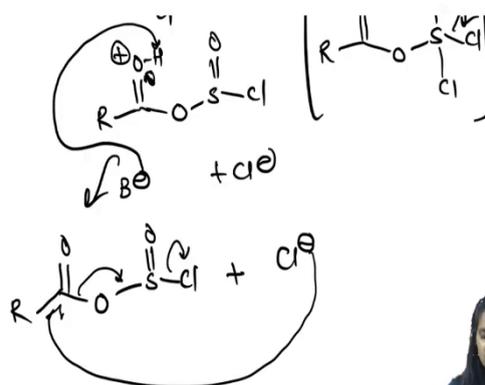
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Now, how do we do that? So, I am going to do two reactions. First, to convert the acids to acid chloride. So, we will start with the carboxylic acid, and we are going to react it with thionyl chloride. Now, remember, this is very similar to the addition elimination reaction that we have seen. Now, the nucleophile is the acid, and electrophile is the sulfur. It has a much higher electrophilic center there.

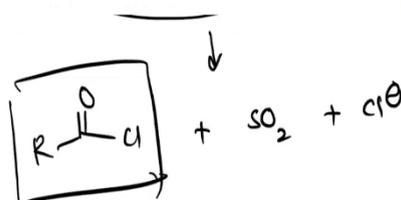
So, in the first step, this nucleophile is going to attack and open this up. What do we have? Now, this oxygen is going to come back kick out a chlorine, forming an intermediate. Typically, this reaction is done in the presence of a base pyridine and thionyl chloride for example, which will also take care of that proton here.

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So, as this proton is lost. So, just a base  $\text{B}^-$ , I am going to write a generic base, it is going to get rid of this. Now, this is my intermediate. Now, in the next step, the chloride is going to come in attack here, and you are going to see a very unusual leaving happening here or leaving group here, because the leaving group that leaves is  $\text{SO}_2$  and  $\text{Cl}^-$ . And  $\text{SO}_2$  here is the leaving group, which is a very good leaving group.

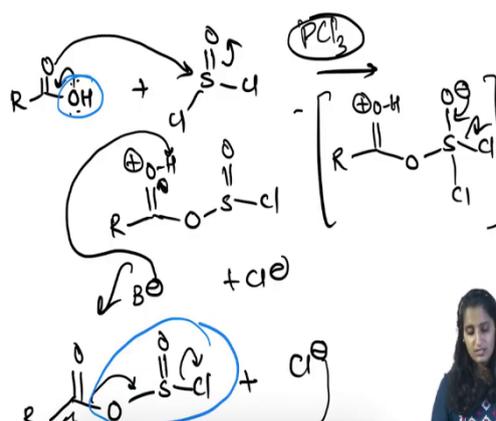
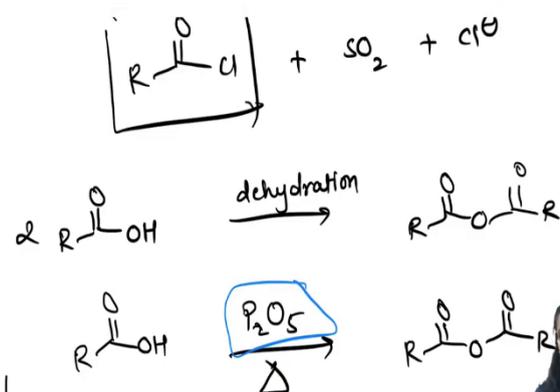
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It leaves as a gas. It is very stable as it leaves, so it is a wonderful leaving group. And that is what really drives this reaction forward is now you have  $\text{RC}=\text{OCl} + \text{SO}_2 + \text{Cl}^-$ . So, what we have here is an acid chloride. And that is how we convert acids to acid chlorides. And we have already seen the reactions of acid chlorides.



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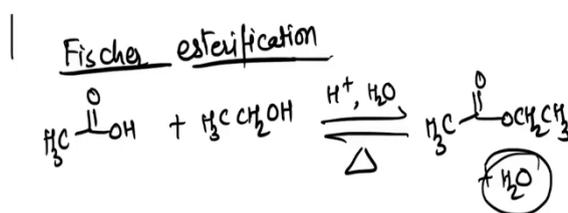


Let us take an acid molecule. Again, I am starting with generic molecule, the R group can be anything ethyl, methyl propyl, so on and so forth. If you take two acid molecules and really remove water, dehydration, what are you going to form? You are going to form an anhydride. And that is the way most anhydrides are formed.

Of course, now, there are better reagents to form anhydrides, but previously, dehydration was a way to really figure out or form anhydrides and the reagent for that is phosphorus pentoxide. So,  $\text{P}_2\text{O}_5$  and heat. So, if you take any acid, put it in  $\text{P}_2\text{O}_5$ , heat it up, you form  $\text{RC}=\text{OOC}=\text{OR}$ . There are many other reagents.

So, even in the case of acid chlorides, instead of a thionyl chloride you can use for example,  $\text{PCl}_3$ , or if you want to form acid bromide, you can use  $\text{PBr}_3$ . So, all of these are alternate reagents and all of them work in a very similar manner in that they convert that OH of the starting leaving group to something that is a much better leaving group. So, in the case of, you know,  $\text{PCl}_3$  and  $\text{PBr}_3$ , also you are going to see the same reactivity. In the case of anhydrides also there are various reagents, but let us just stick to one that really works well, it is the  $\text{P}_2\text{O}_5$ .

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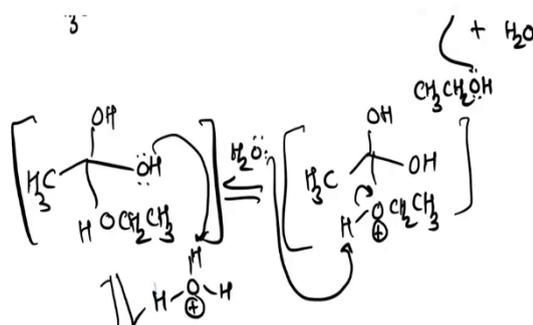
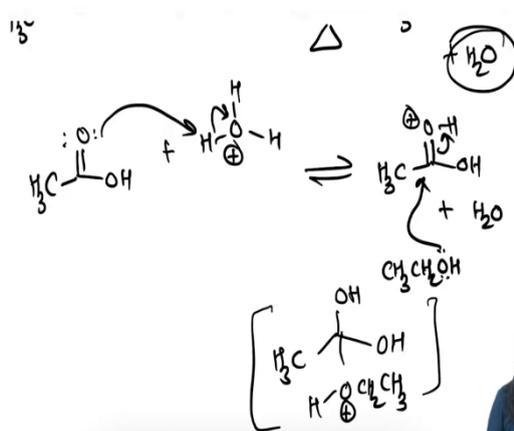


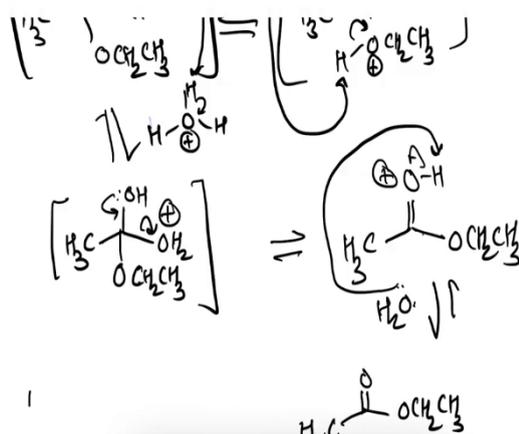
That is about that conversion of acids to acid chlorides and anhydrides. Now, let us look at a reaction that is done very usually to convert acids into esters. And, of course, to form the esters, we have seen that you can either form anhydrides or chlorides and then react them with alcohol to form the esters, but here is a reaction that is very often done which is called as Fischer esterification, is done by ML Fischer. And we are going to do this reaction not in a basic condition, but it happens in an acidic condition, so we are going to start with a generic acid. Instead of generic let us take a particular example. So, let me start with acetic acid and let us start with ethanol.

Now, both of these when reacted together in the presence of  $\text{H}_2\text{SO}_4$  and heat, so we need some mineral acid also, mineral acid and some water, so it is going to be  $\text{H}_3\text{O}^+$  mainly. And when we heat it when we reflux it, remember it is going to form the Ester. So, let me just rewrite this condition.

Now, it is a reversible reaction, meaning the ester that you form, which is the ester here, it can go back to the starting alcohol and acid. So that is why we do various different steps, such that we drive the reaction forward to the esterification. So, if we are interested in ester, then we kind of drive the reaction forward by taking larger quantities of acids and alcohols. In fact, sometimes we take twice the amount of alcohol because it even acts as a solvent for the reaction, and we heat it up, we remove water. So, there is a water molecule that gets kicked out. And this water is constantly removed from the system such that the ester formation is favored.

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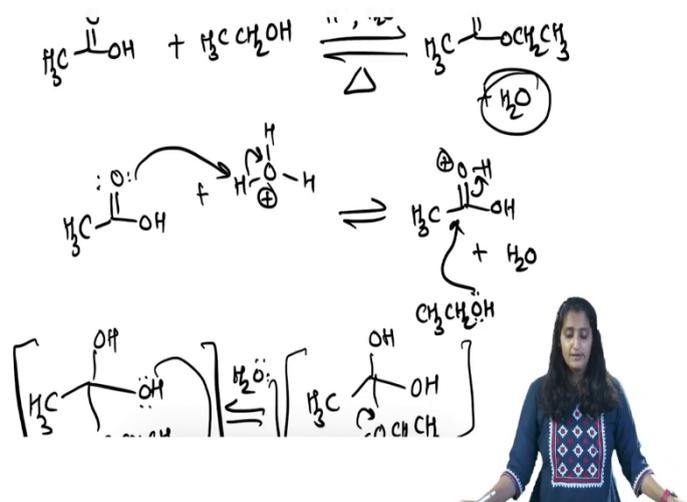


So, now let us try to do the mechanism of this particular reaction. So, let us take acetic acid. In the case of acetic acid being mixed with  $\text{H}_3\text{O}^+$ , what is the first step? Remember, the oxygen here is going to get protonated, and we will form this and water. Now, we have ethanol as our nucleophile, here. It is going to attack it here, open it up. Again, you have a tetrahedral intermediate. So, remember, most of the reactions that we do in this particular chapter are same way, addition, form the tetrahedral intermediate and then you later eliminate.

This is my intermediate, it is going to lose out the proton because we have water here in the solution, this is the real intermediate which is neutral. Now, what we are going to do is, see, our aim is to form the ester. So, in order for the ester to form we have to kick out any of these two OH's and they are both equivalent. So, in order to kick them out in the acidic condition as we were talking about we are now in the acidic conditions, it is not easy to kick out  $\text{OH}^-$  as a leaving group. So, we need to make it into a better leaving group by reacting it with  $\text{H}_3\text{O}^+$ .

So, let us make this into a good leaving group and we form this. And as it forms a good leaving group you can kick it out reforming the bond here, really forming the ester and of course, it is going to later lose a proton to form the final product, forming the final ester.

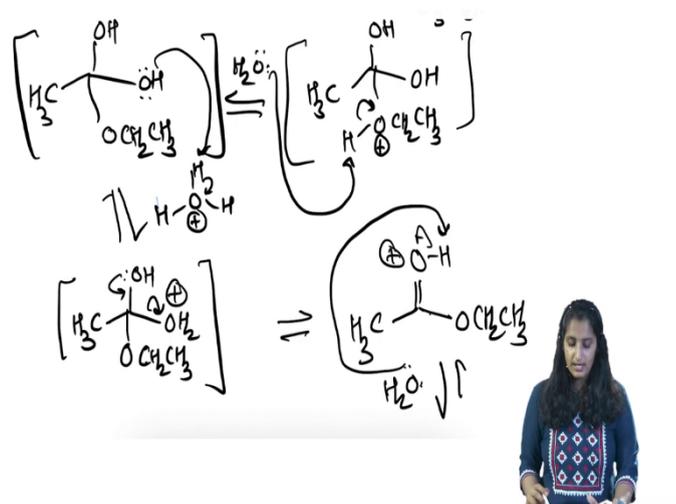
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Now, as I said that this Ester formation, Fischer esterification reaction is quite often used to create esters of a choice. In fact, we have also shot a video of this being synthesized in the lab. So, you can have a look at it, we will include it as one of the resources in this week, you can actually see how esters are prepared in the lab.

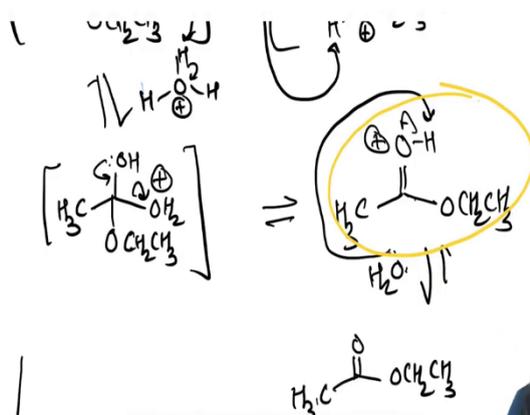
Now, remember that esters can also undergo hydrolysis, so you can start with an ester and then go backwards to the corresponding acids and alcohol. And that is going to be a homework question for you guys wherein you start try writing the mechanism wherein you start from the ester and then you form the corresponding alcohol and acid.

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Remember that each of the intermediates that we form in this particular reaction will still form in the backward reaction also. So, this is called as the principle of microscopic reversibility wherein when you are trying to write down the mechanism for a backward reaction, the same intermediates are going to form although arrow pushing is going to change.

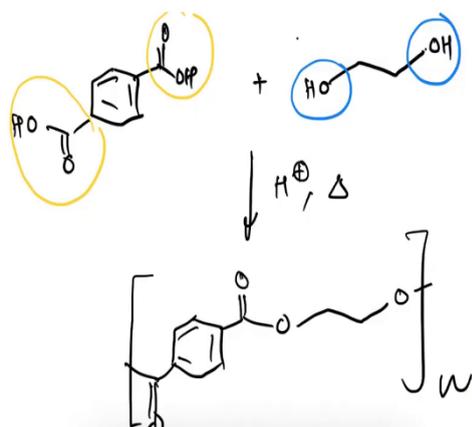
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Just for explanation, the first step for the reverse reaction, wherein we start from the ester is going to be protonating that carbonyl oxygen to form this particular intermediate here. So, the idea is that you form the same intermediate. So, it is like if you are going from one place to another, let us say, from Bombay to Pune and if Lonavala comes in between, while going back from Pune to Bombay, you are still going to have to go through Lonavala.

Although, the route will be different, like in one case you are going backwards, in the other case, you are going forwards. So, that is the principle of microscopic reversibility. And I really want you to try writing the mechanism of a reversible reaction. And depending on what we favor, we can change the condition of the reaction as if we want to hydrolyze an ester, just add in a lot of water, if we want to form an ester just remove a lot of water.

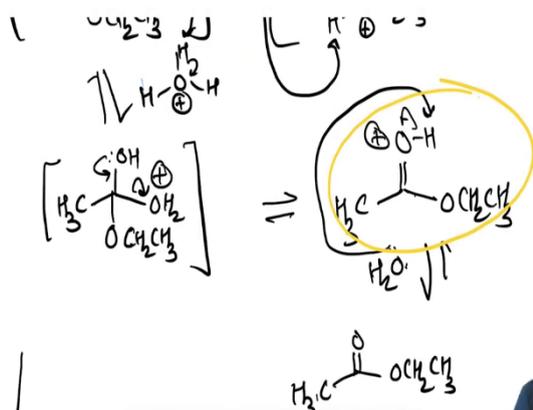
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Now, this esterification reaction is, as I was saying, it is quite widely used in industry. And one of the ways Dacron or Terylene polymer is made, is using this reaction. So, for that, what you do is, you start with Terephthalic acid. And you start with ethylene glycol. As you can see, I have two acid functionalities. One here, one here on the same molecule, and I have two alcohol functionalities. And thus, it is going to link to form a polymer.

And when these two react together, in the case of mineral acids and heat, what you are going to form is you're going to form the corresponding Dacron polymer. So, let me just draw. So that becomes your unit, and this chain is going to react repeat again and again creating a long polymer which we can use. And that is how Terylene is formed. I thought this would be an interesting everyday example for esterification. And you can see how by adding two functionalities, we can now convert any ester into a polyester kind of role. And that is how most of the polyesters are actually made.

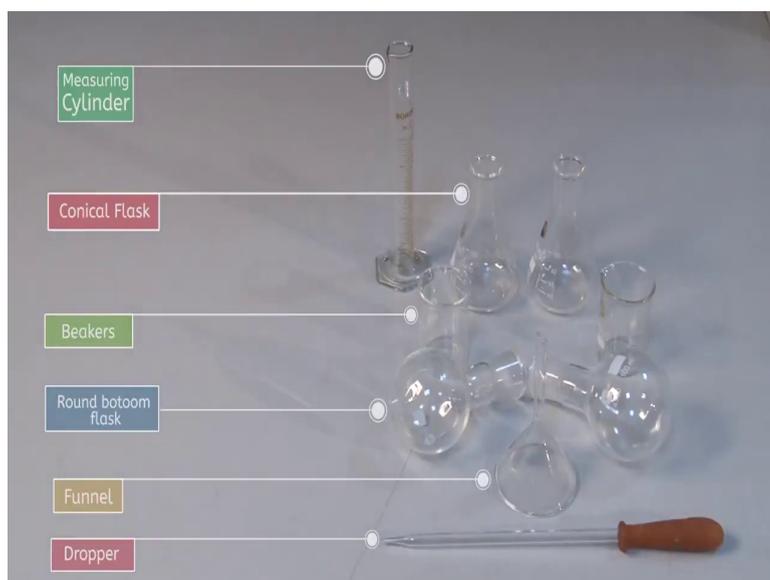
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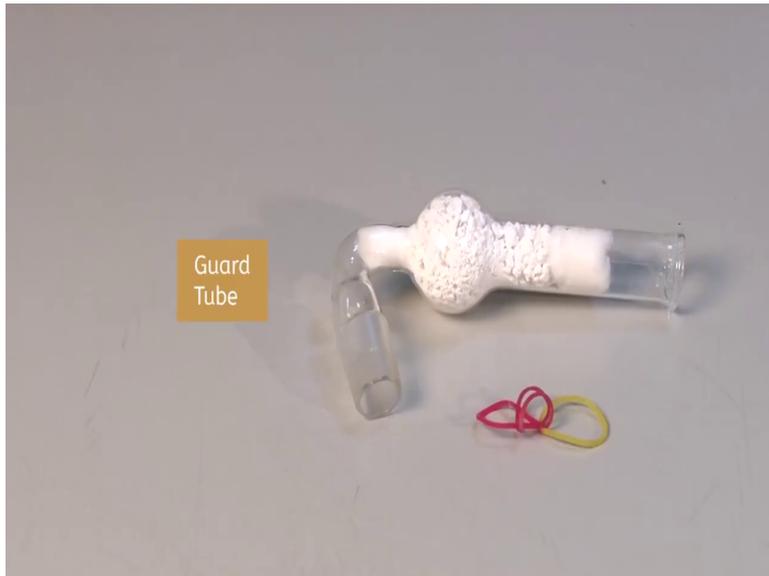


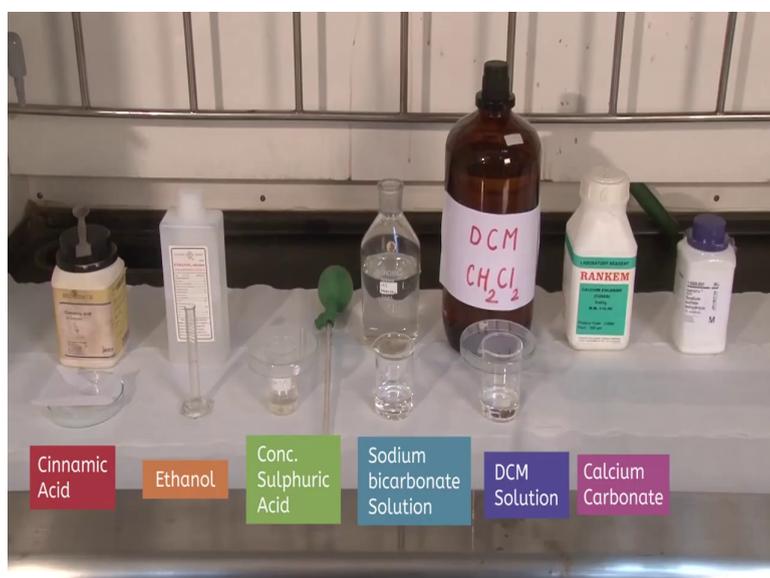
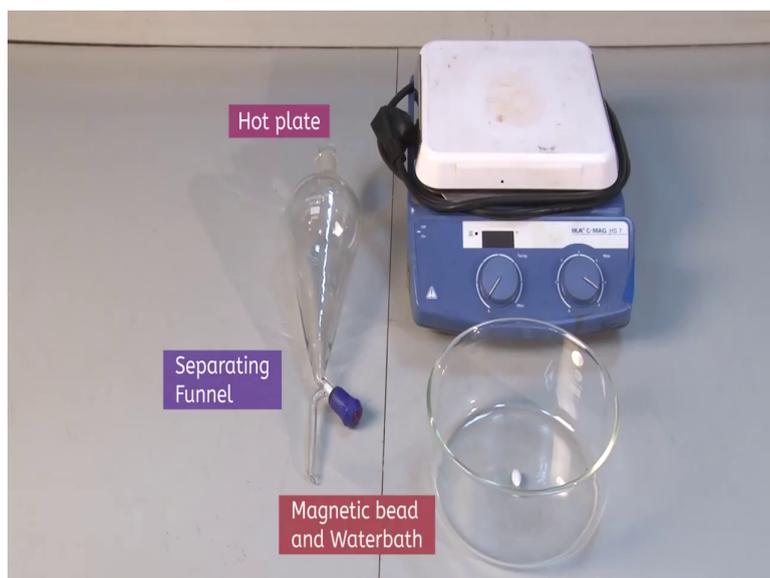
So, that is how the certification is done, and do check out the reaction being done in lab. Thank you.

Speaker 2: We get fascinated by the odors and flavors of flowers and fruit. But have you ever wondered what plays the important role? The outcome is a result of complex mixture of many chemical compounds interacting with our olfactory sensors. It was discovered that, there was generally one group of compounds in common, known as ester. Ester can be prepared by reacting carboxylic acid with alcohol under acid catalysis. Today, we will prepare cinnamate that smells like cinnamon.

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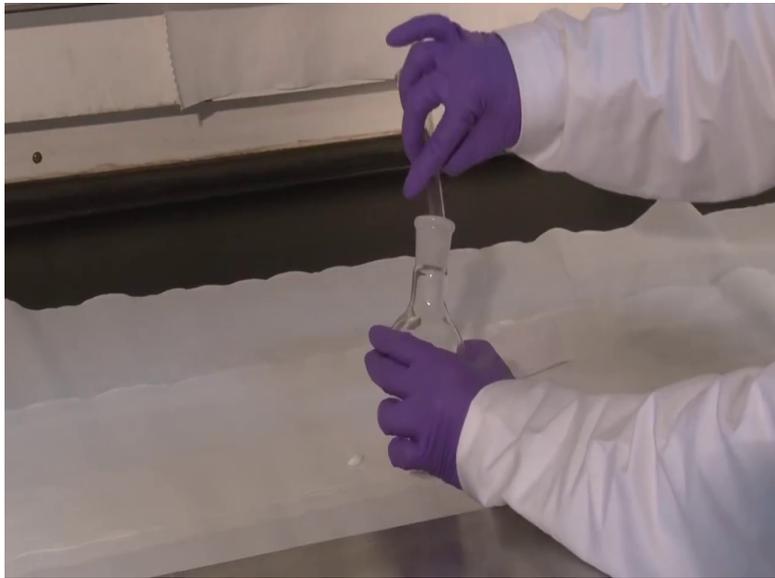


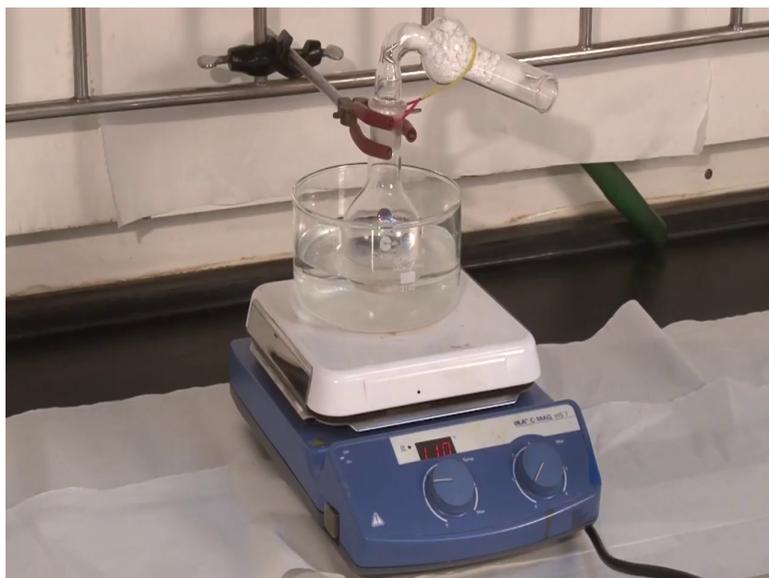




In this experiment, we will need. Also, we need a rotary evaporator and a magnetic stirrer hot plate. The chemicals required in this experiment are cinnamic acid, ethanol, conc sulphuric acid, sodium bicarbonate solution, DCM, calcium carbonate, sodium sulphate...

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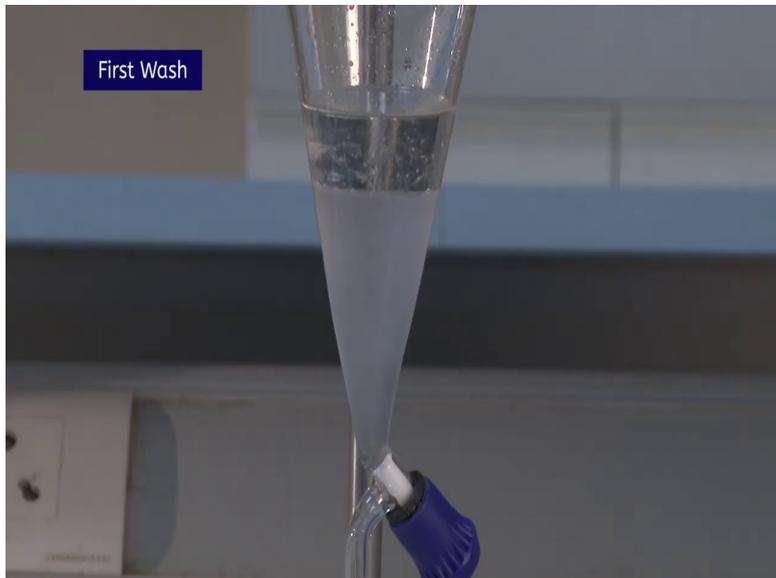




Let us start with adding cinnamic acid, ethanol and magnetic bead in a round bottom flask. Also add few drops of concentrated sulfuric acid to the reaction mixture. It not only acts as a catalyst, but also as a dehydrating agent to drive the equilibrium forward in order to obtain ester. Now, let us set up the reaction apparatus. Heat the reaction mixture using water bath for 1 hour. So, though we obtain product, there may be possibility that some amount of acid and alcohol might not have reacted.

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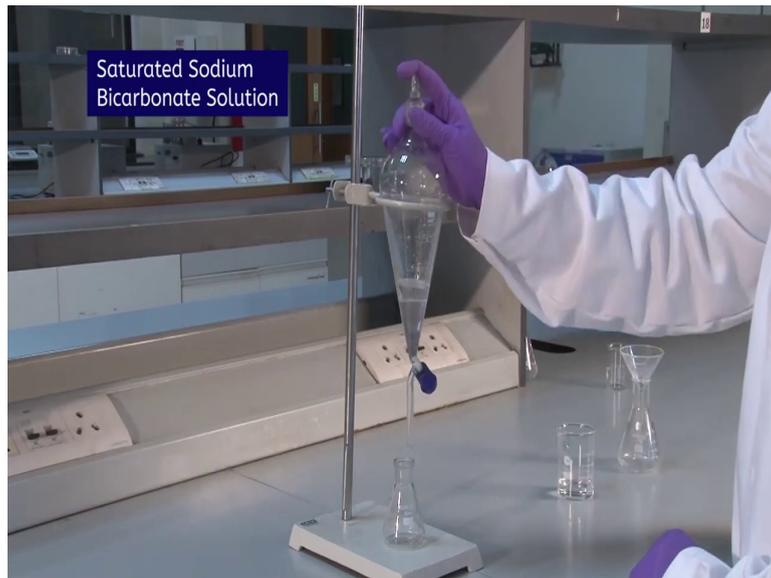
To extract ester, we will start by adding DCM as a common solvent. To remove alcohol, we wash the reaction mixture with water. As DCM is denser than water we are interested in lower layer. We collect the DCM solution in a conical flask, collect the unwanted solution in another conical flask.

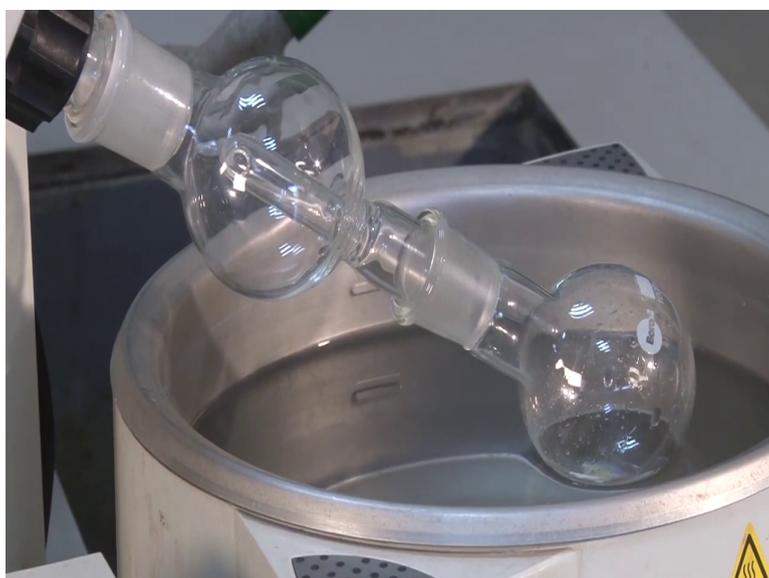
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Repeat washing the reaction mixture for three times so that no left alcohol is present.

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Now, wash the organic layer with saturated sodium bicarbonate solution, so that unreacted cinnamic acid gets separated. Sodium sulfate is added to ensure that no unwanted mixture is left in the solution. We separate the mixture using gravity filtration. We have ester, but dissolved in ether. How do we separate it? We separate them by rotary evaporation.

We finally obtained ethyl cinnamate. You can prepare different esters of different odor by using various combination of carboxylic acid and alcohol. It is surprising that though esters have very pleasant odor, but they are not generally used as perfume. Esters in contact with sweat hydrolyzed to form carboxylic acid and alcohol which generally smell foul. Hope you liked the video. Thanks for watching.