Introductory Organic Chemistry
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Lecture - 48
Alcohols Part - 03

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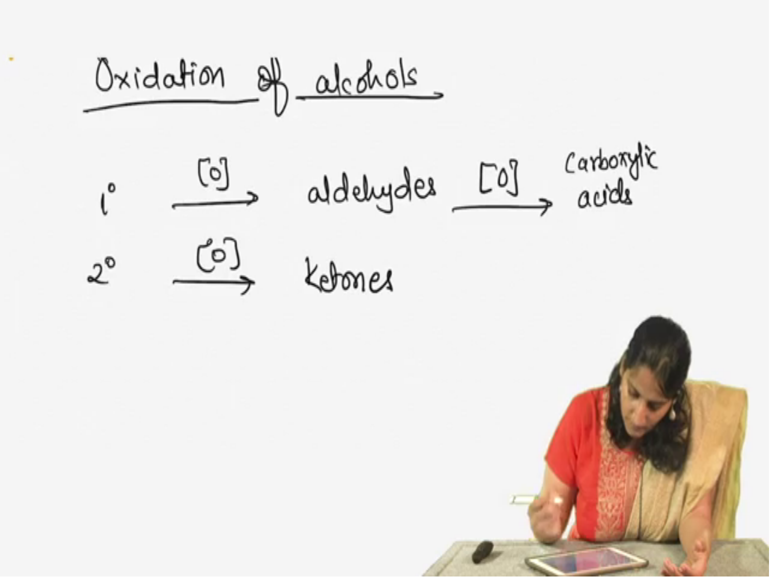

Oxidation of alcohols

$1^\circ \xrightarrow{[O]}$ aldehydes $\xrightarrow{[O]}$ carboxylic acids

$2^\circ \xrightarrow{[O]}$ ketones

The next type of alcohol reaction that we want to talk about are oxidation reaction. So, the next reaction that I want to talk is oxidation. So, primary alcohols can be oxidized to aldehydes and which can in turn be oxidized to carboxylic acids depending on the experimental conditions of course; whereas, secondary alcohols only go up to ketones and tertiary alcohols cannot be oxidized, right.

So, I am going to write this down primary upon oxidation will give you aldehydes which upon oxidation will give you carboxylic acid, okay. Secondary upon oxidation will give you corresponding ketones whereas tertiary, no reaction, okay.

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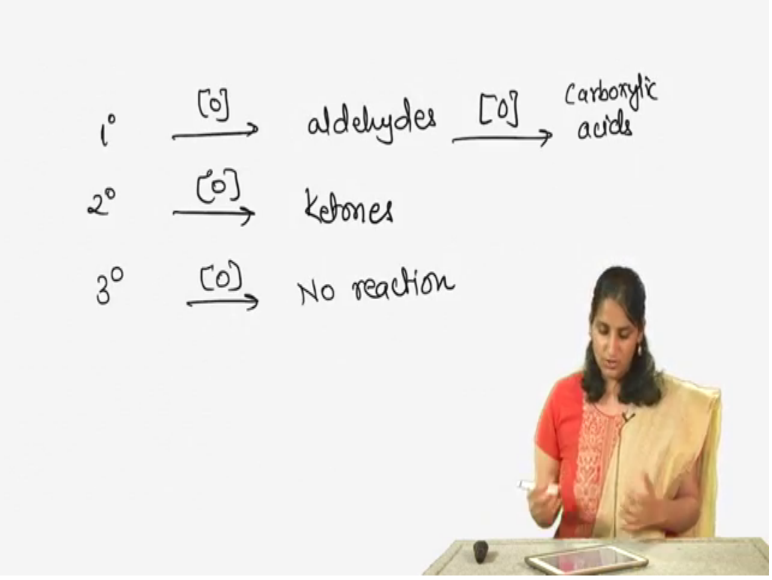

So, again this is one of the cases where whether the alcohol is primary, secondary or tertiary place a huge difference in the kind of products that is formed. Now, the reagent that is most commonly used to convert primary alcohols to carboxylic acids is chromic acid or H_2CrO_4, right.

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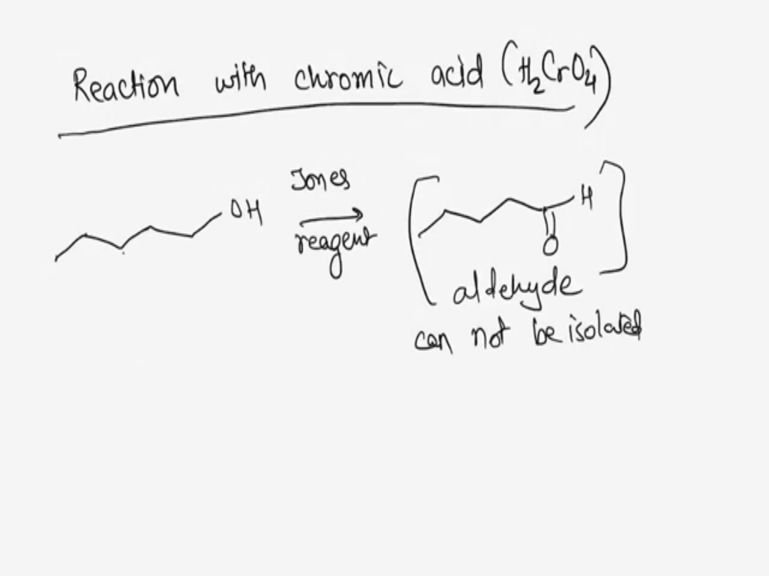

And H_2CrO_4 or chromic acid is really prepared by dissolving either chromium oxide or potassium dichromate in aqueous sulphuric acid, right, and if you mix chromic acid with sulphuric acid it is most commonly known as Jones reagent.

So, you will also see Jones reagent written instead of chromic acid, but it is just a reagent to oxidize an alcohol all the way to carboxylic acid, right. So, let's take for example, so, this is 1-pentanol and if you react it with Jones reagent, the reaction goes through an intermediate of an aldehyde; however, this aldehyde cannot be isolated, okay. The aldehyde that is not isolated immediately reacts with the Jones reagent that is present to form the corresponding carboxylic acid, okay.

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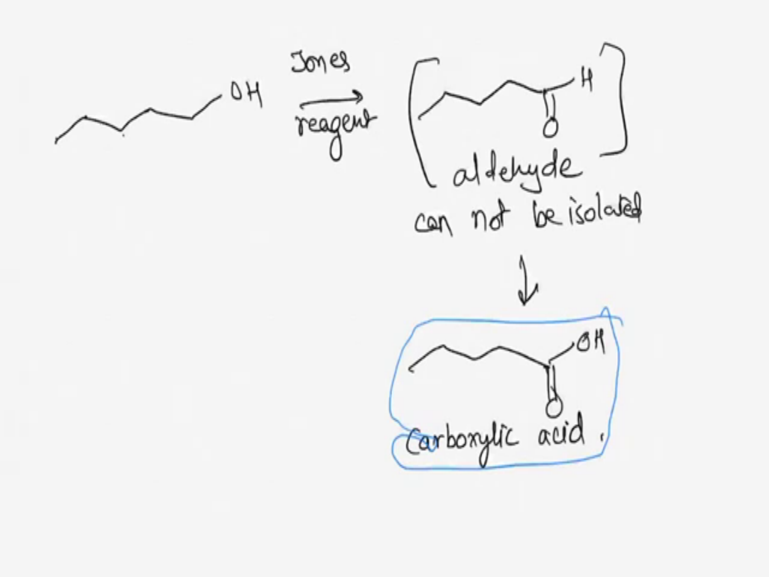

And what we really isolate in the reaction is the final product as the carboxylic acid. So in fact, when primary alcohols react with Jones reagent it's kind of an all the way through train and there is no middle stop at the corresponding aldehyde. Secondary alcohols using chromic acid or Jones reagent will form the corresponding ketones.

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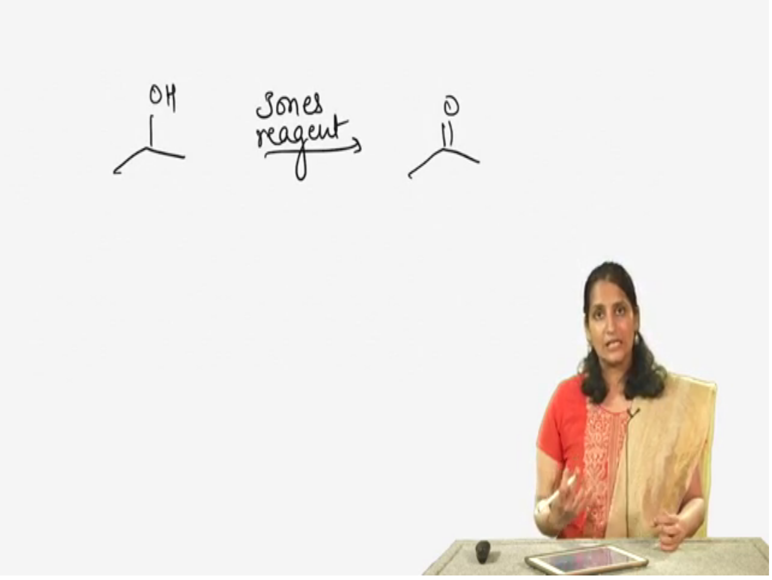

So, if I take isopropanol and if I put it in Jones reagent, it will form the corresponding ketone. And whereas, tertiary alcohols do not get oxidized, that is because tertiary alcohols the oxygen is attached to a carbon that has three other carbons attached to it. So, it cannot form an additional carbon-oxygen bond and thus tertiary alcohols will be resistant to even the strongest oxidizing agents and will not get oxidize.

So, now, the question arises, what if I want to form that aldehyde? Jones reagent won't be useful. So, the other kind of reagent that is useful is called as pyridinium chlorochromate or PCC.

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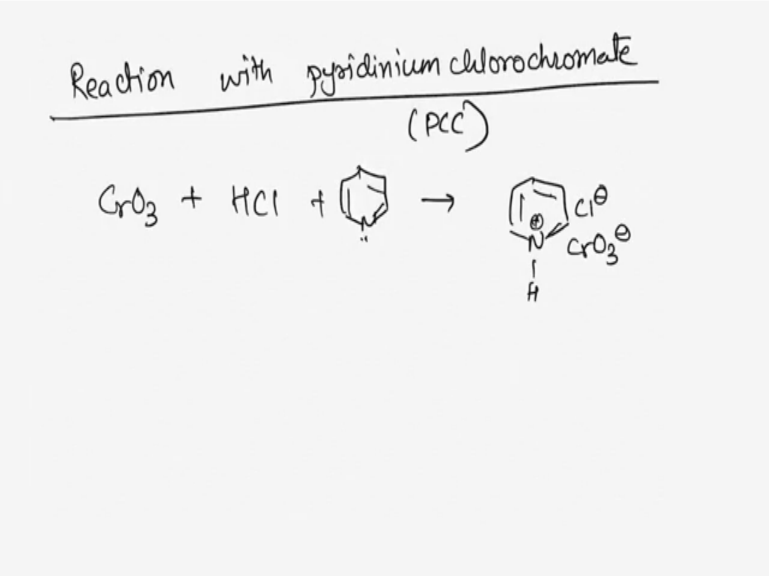

And here in PCC is made by dissolving CrO_3 and aqueous HCl and then adding pyridine to it. So, that's how the pyridinium chlorochromate is formed.

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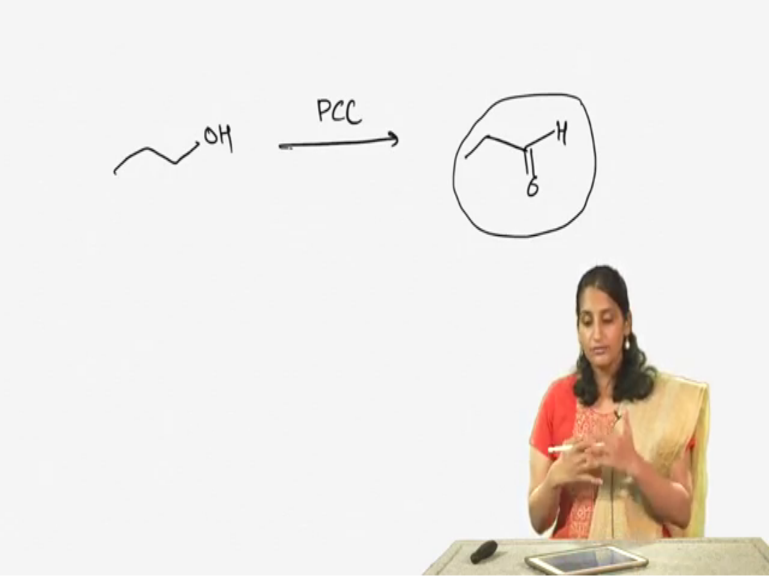

And now let us look at a reaction of 1-propanol and if you react it with PCC, then especially at low temperature it is going to stop the reaction to form that propionaldehyde. And in fact, this is the product that gets isolated and the reaction does not go all the way to carboxylic acid, okay. It is one of the most chosen reagents because PCC selectively works for oxidation of primary alcohols.

It does not affect any other functional groups in the molecule, especially functional groups such as carbon-carbon double bonds or even other easily oxidizable functional groups they will not react with PCC; PCC is very specific to oxidation of primary alcohols to the corresponding aldehydes, okay. Now, PCC does not oxidize aldehydes further that is because PCC is mainly not used in water, but it is used in organic solvent like dichloromethane.

Now, without water this aldehyde cannot really form something called as a hydrate and that hydrate is responsible for the formation of carboxylic acid, but since you are not in water you cannot form hydrate you can isolate the product that stops at the aldehyde stage, okay.

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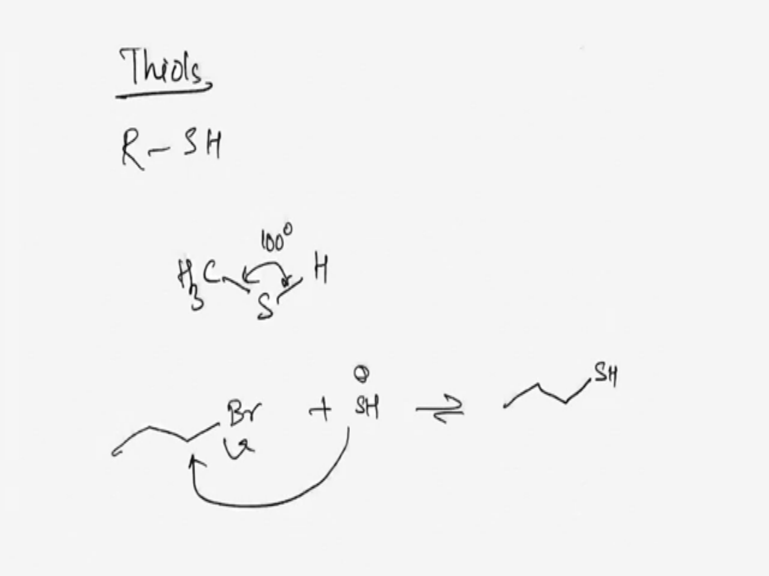

So, that was about alcohols. Now, I also want to talk a little bit about thiols, though we are not going to look at the chemistry of thiols a lot, it is important to talk about thiols because thiols are again seen very widely in the biological world, right. So, the functional group of thiols is R-SH, right and very similar to ROH, if you remember sulfur is one row down as compared to the oxygen in the periodic table. But, because of this what happens is that sulfur is quite bigger in size as compared to oxygen and this will have some implications on the bonding in the case of thiols. It will also have some implications on the way thiols react, it will be a little different from how alcohols react.

If you really look at the bond angle which is carbon-sulfur-hydrogen bond angle, let's take methanethiol for example, okay. If you look at this bond angle, the bond angle here is close to 100 degrees, okay. If you remember the bond angle in the case of alcohols it was 108 or close to 109.5 degrees, right and 100 is in fact, quite deviated from that 109.5.

So, if sulfur was really forming all sp^3 hybridized orbitals and forming kind of bonds such that sulfur was fully sp^3 hybridized, then having a bond angle of 109.5 would be suitable. However, we see a bond angle close to 100 meaning the hybridization of sulfur is not exactly sp^3.

In fact, it has considerably more p character because if it was all just unhybridized 3 p-orbitals then the bond angle would be close to 90 degrees. But since it is not 90, it is not 109, in fact, it is somewhere in between which is 100. It can be said that it has hybridized but it has the bonding, has considerable more amount of p character than a regular sp^3 hybridized orbital, okay.

Now, one of the most outstanding or a most known physical characteristic of low molecular weight thiols is their smell and in fact, it is one of the most notorious smells you can call it and that’s why thiols are kind of difficult to work with as well.

Now, you might have heard about skunks. So, skunks are these animals that are found in North and South America and these skunks are well known for their stinky smell. In fact, if it is afraid or if it has to attack it has that ability to spray a liquid with a very unpleasant and strong smell.

And in fact, the main compounds that are found in a skunk spray, that they use to spray on an attacker, are all thiol molecules. And that’s why as I said the main physical characteristic of low molecular weight thiols is their smell. In fact, you must have heard about mercaptan, it is an additive that is added to natural gas because natural gas does not smell on its own. So, mercaptan is added in small quantity such that if there is a gas leak you can actually smell the gas, right. So, mercaptan is another small molecular weight thiol that is added to your regular natural gas.

Now, if you think about the polarity of sulfur-hydrogen bond it is not as highly polar as oxygen-hydrogen bond, right; because oxygen is much more electronegative than sulfur, there is a huge polarity associated with the OH bond. Whereas, for the SH bond it is not as polar. And as a result thiols will show very little association for hydrogen bonding. We have seen that the boiling points of alcohols are really high, because alcohols tend to engage in hydrogen bonding and the cumulative effect of all these hydrogen bonds really makes the boiling point go up.

In the case of thiols on the other hand there is not much hydrogen bonding present and thus you don’t see the boiling points of the thiols being really high as compare to alcohol. In fact, to compare water H_2O has a boiling point of 100, whereas, H_2S is gaseous at room temperature. So, that really gives you the comparison of the hydrogen bonding that happens in the case of water versus in the case of H_2S and the association with hydrogen bonding in each case.

Another thing to notice is that hydrogen sulphide is much more acidic than water. For example, water's pKa is around 16 whereas, H_2S has a pKa very close to 7. Now, why H_2S has a lower pKa? If you remember the conjugate base of water is OH^- whereas, the conjugate base of hydrogen sulphide is SH^- and SH^-, big sulfur because of it is really large size can stabilized that negative charge very well. And thus the conjugate base of H_2S is much more stable making it much more acidic, right.

So, if I want to extrapolate the same property, thiols are stronger acids than alcohols, right. So, for example, if we compare the pKa values of ethanethiol and ethanol; ethanol as we know has a pKa value close to 16, whereas ethanethiol has pKa value close to 10. So, the corresponding thiols are stronger acids than alcohols, okay. So, I don't want to go over reactions of thiols per se, but one of the reactions to make thiols is by S_N2 reaction, right.

So, we have just seen it previously in the same lecture is that you can take an alkyl halide and react it with SH^- to form the corresponding thiol, right. And S_N2 chemistry is a very good way to form the corresponding thiols because SH^- is a very good nucleophile. The other chemical reaction or a chemical property of thiol really comes from the fact that sulfur atom can be oxidized into various different higher oxidation states. So, you must have seen sulfur-sulfur bonds, right or you must have seen other oxidation states of sulfur and all of these can be done by selectively reacting the sulfur compounds in a particular reaction.

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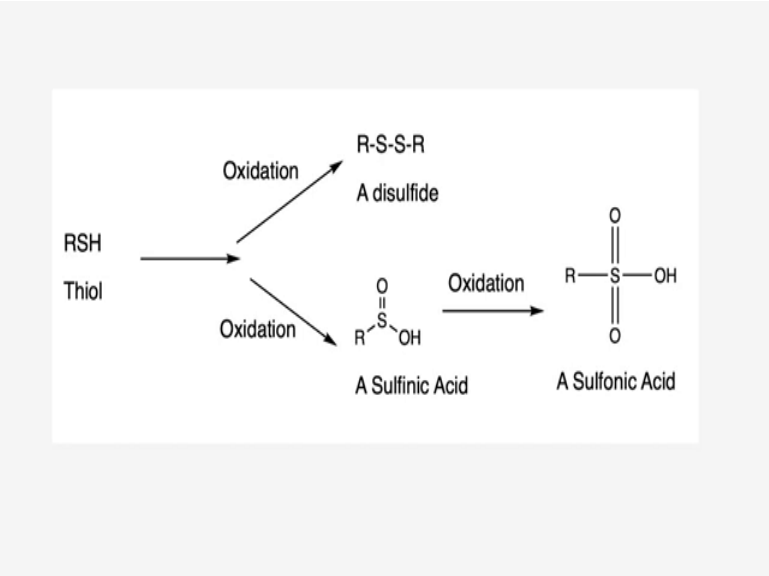

So, in fact look at this diagram which shows the various oxidation states of sulfur. Out of these the most common oxidation-reduction reaction of sulfur compounds in biological systems is inter-conversion between a thiol and a disulfide. In fact, molecular oxygen can convert a thiol to a disulphide under biological conditions. And the disulfide bond is one of the more important structural features that is responsible for stabilizing the tertiary structure of many proteins, and thus this reaction of thiol getting converted to a disulfide bond is of biological importance, okay. So, that was about thiols.

Next class we will talk about chemistry of ethers, epoxides and aromaticity.