

Semester – IV MJC – 6(T) Organic Chemistry
Unit – I Alcohols, Phenols , Esters and Epoxides

Esterification Lucas Test and Oxidation of Alcohol

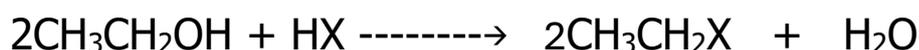
The Reaction between Sodium Metal and Ethanol

If a small piece of sodium is dropped into ethanol, it reacts steadily to give off bubbles of hydrogen gas and leaves a colorless solution of sodium ethoxide $\text{CH}_3\text{CH}_2\text{ONa}$. The anion component is an *alkoxide*.

If the solution is evaporated carefully to dryness, then sodium ethoxide ($\text{CH}_3\text{CH}_2\text{ONa}$) is left behind as a white solid.



The Reaction between Alcohol and Alkyl halide The Lucas test, using a mixture of concentrated hydrochloric acid HCl and anhydrous zinc chloride (ZnCl_2), differentiates alcohols (R-OH) by converting them into insoluble alkyl chlorides (R-Cl). The reaction produces immediate turbidity for 3° alcohols, turbidity within 5-10 minutes for 2° alcohols, and no turbidity at room temperature for 1° alcohols



The reaction takes place through SN_1 mechanism except for methanol and 1° alcohols.

Order of reactivity of alcohols: $3^\circ > 2^\circ > 1^\circ$

Order of reactivity of hydrogen halides: $\text{HI} > \text{HBr} > \text{HCl}$

Lucas test: A solution of anhydrous zinc chloride and concentrated hydrochloric acid is called Lucas reagent. This reagent is used to distinguish 3° , 2° and 1° alcohols. When alcohols are added to the solution of Lucas reagent in 1:1 ratio and the resulting mixture is shaken an insoluble alkyl halide is formed. This insoluble alkyl halide forms at a different speed with 3° , 2° and 1° alcohols, thus this reaction can be used to distinguish them. A 3° alcohol on reaction with Lucas reagent forms the respective alkyl halide immediately to form turbidity. 2° alcohols react in some time to form turbidity and 1° alcohols give no turbidity.

Esterification: When alcohols react with carboxylic acids in the presence of concentrated sulphuric acid they give esters. We can define esterification as the process which involves combination of an organic acid (RCOOH group) and an alcohol (ROH group) that leads to the formation of an ester (RCOOR group) and water.

The five steps involved in the process of esterification are:

Step 1: Formation of cation:

We must know that the carbocation is formed by abstracting one hydrogen.

Step 2: Delocalization of carbocation:

When the carboxyl oxygen gets protonated it gives delocalized carbocation which makes this carbocation a better electrophile.

Step 3: Transfer of proton:

After the delocalization of carbocation a proton is transferred to one of the hydroxyl groups. Thus, forms a good leaving group in the reaction.

Step 4: Removal of water molecule:

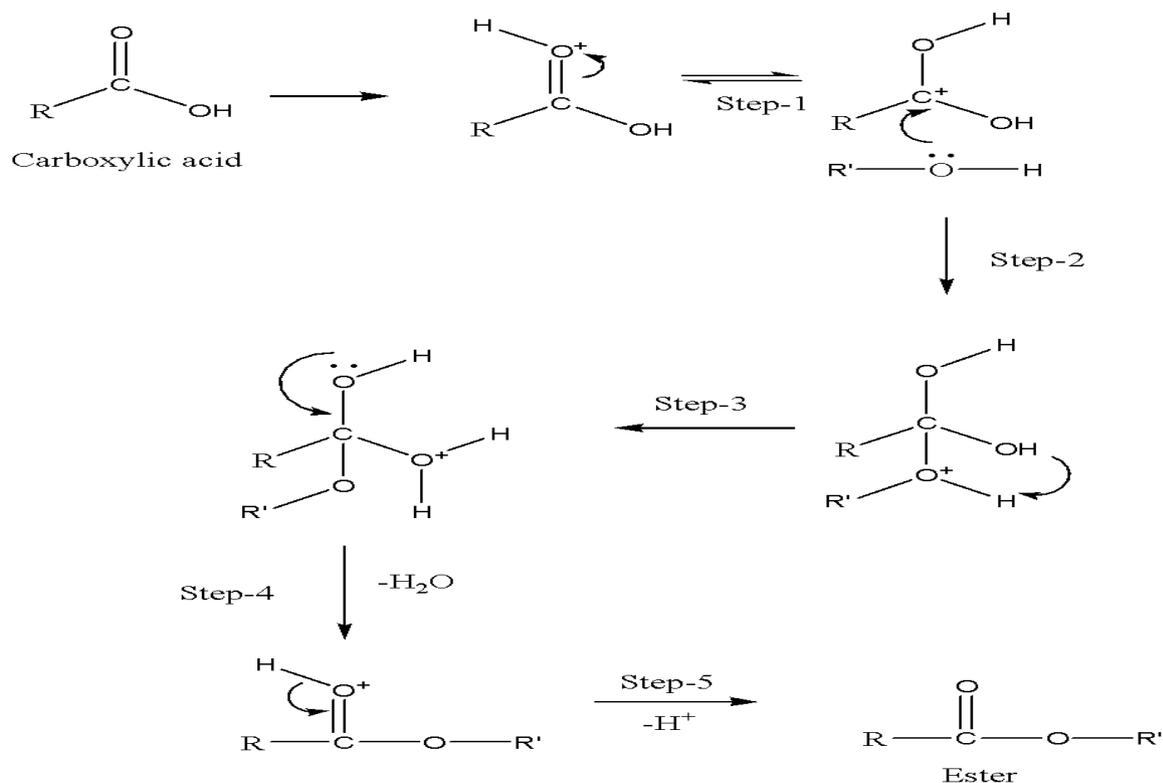
In this step, the hydroxy group's of alcohol oxygen atom donates a pair of electrons to a carbon atom which makes a pi-bond by eliminating water. The concentration of water is less than methanol.

Therefore, it is not a feasible nucleophile to reverse this reaction.

Step 5: Formation of ester:

At last, ester formation takes place by the elimination of hydrogen.

We can write the overall mechanism as,



Oxidizing the different types of alcohols

The oxidizing agent used in these reactions is normally a solution of sodium or potassium dichromate(VI) acidified with dilute sulfuric acid. If oxidation occurs, then the orange solution containing the dichromate(VI) ions is reduced to a green solution containing chromium(III) ions. The electron-half-equation for this reaction is as follows:

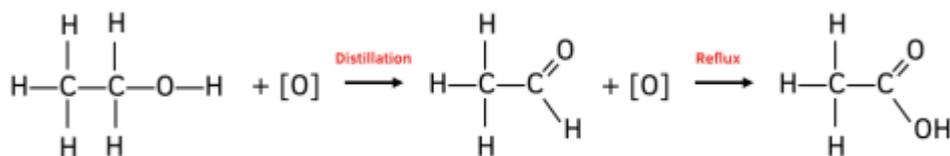


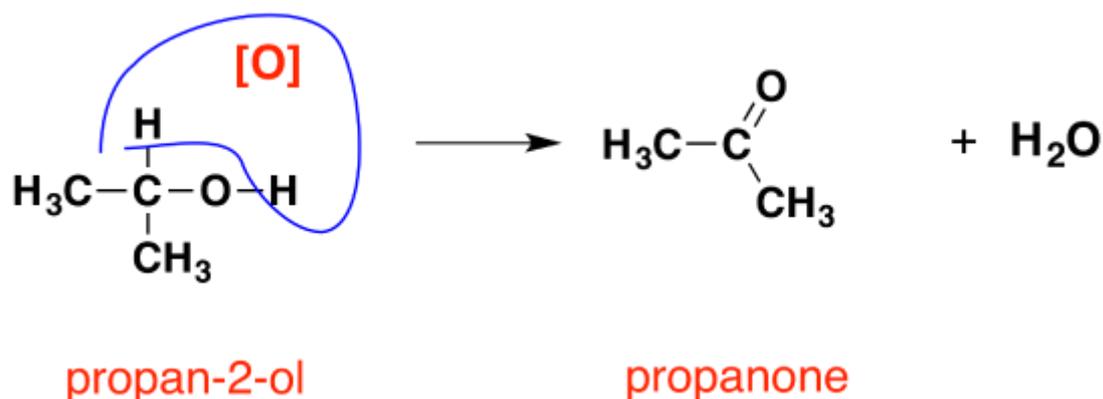
Fig 1. Oxidation of Primary Alcohols.

Primary alcohols can be oxidized to either aldehydes or carboxylic acids, depending on the reaction conditions. In the case of the formation of carboxylic acids, the alcohol is first oxidized to an aldehyde, which is then oxidized further to the acid.



↑
this means "oxygen from an oxidizing agent"

Secondary alcohols are oxidized to ketones - and that's it. For example, if you heat the secondary alcohol propan-2-ol with sodium or potassium dichromate(VI) solution acidified with dilute sulfuric acid, propanone is formed. Changing the reaction conditions makes no difference to the product. Following is the simple version of the equation, showing the relationship between the structures:



Tertiary alcohols are not oxidized by acidified sodium or potassium dichromate(VI) solution - there is no reaction whatsoever. If you look at what is happening with primary and secondary alcohols, you will see that the oxidizing agent is removing the hydrogen from the -OH group, and a hydrogen from the carbon atom is attached to the -OH. Tertiary alcohols don't have a hydrogen atom attached to that carbon.

You need to be able to remove those two particular hydrogen atoms in order to set up the carbon-oxygen double bond.

