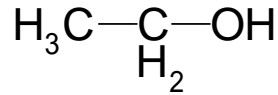


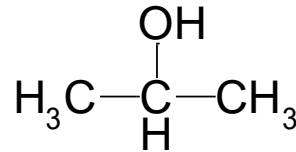
# Alcohols

Alcohol have the functional group – OH attached to a hydrocarbon chain. They are relatively reactive.

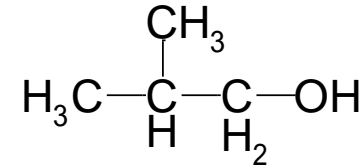
Some Examples:



Ethanol



Propan-2-ol



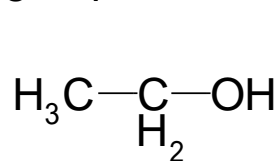
2-methylpropan-1-ol

## The different kinds of alcohols

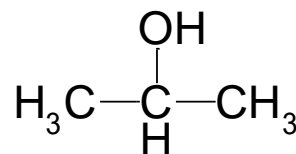
Alcohols fall into different classes depending on how the -OH group is positioned on the chain of carbon atoms. There are some chemical differences between the various types. The three examples above are all examples of **PRIMARY ALCOHOLS**.

# Primary Alcohols

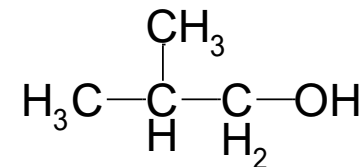
In a primary ( $1^\circ$ ) alcohol, the carbon which carries the -OH group is only attached to one alkyl group.



Ethanol



Propan-2-ol



2-methylpropan-1-ol

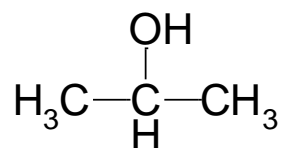
Notice that it doesn't matter how complicated the attached alkyl group is. In each case there is only one linkage to an alkyl group from the CH<sub>2</sub> group holding the -OH group.

There is an exception to this. Methanol, CH<sub>3</sub>OH, is counted as a primary alcohol even though there are no alkyl groups attached to the carbon with the -OH group on it.

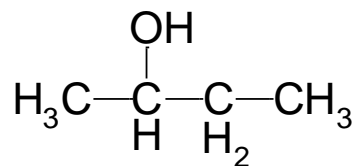
# Secondary + Tertiary Alcohols

In a secondary ( $2^\circ$ ) alcohol, the carbon with the -OH group attached is joined directly to two alkyl groups, which may be the same or different.

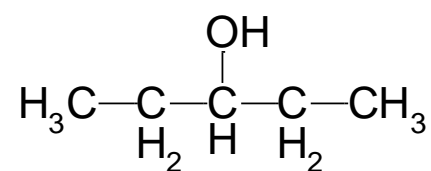
Examples:



Propan-2-ol



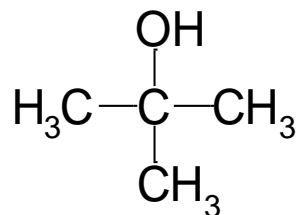
Butan-2-ol



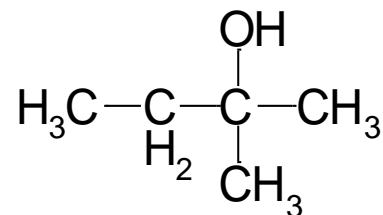
Pentan-3-ol

In a tertiary ( $3^\circ$ ) alcohol, the carbon atom holding the -OH group is attached directly to three alkyl groups, which may be any combination of same or different.

Examples:



2-methylpropan-2-ol



2-methylbutan-2-ol

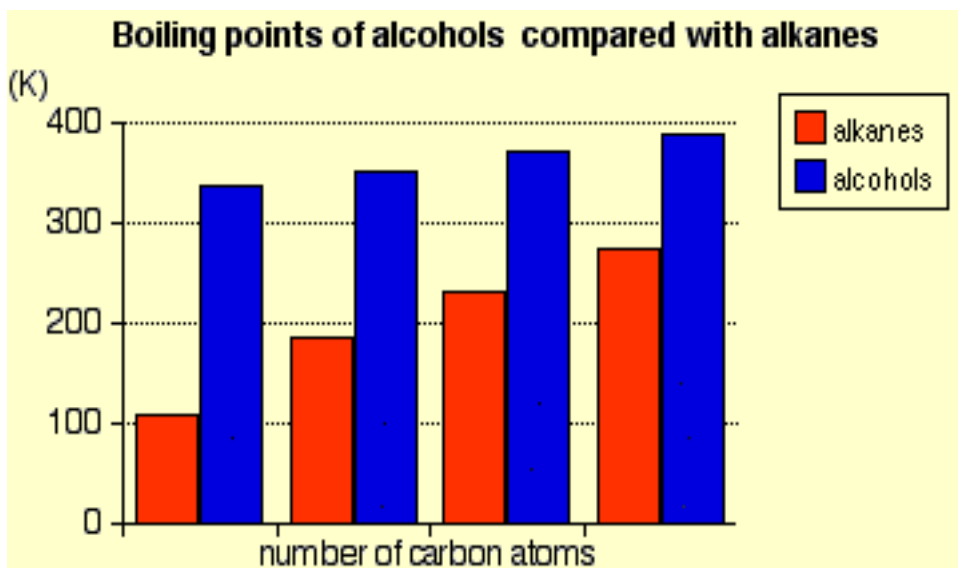
# Properties of Alcohols

## Boiling Points

The chart shows the boiling points of some simple primary alcohols with up to 4 carbon atoms.

They are: Methanol Ethanol Propan -1- ol Butan -1- ol

They are compared with the equivalent alkane (methane to butane) with the same number of carbon atoms.



Notice that:

- The boiling point of an alcohol is always much higher than that of the alkane with the same number of carbon atoms.
- The boiling points of the alcohols increase as the number of carbon atoms increases.

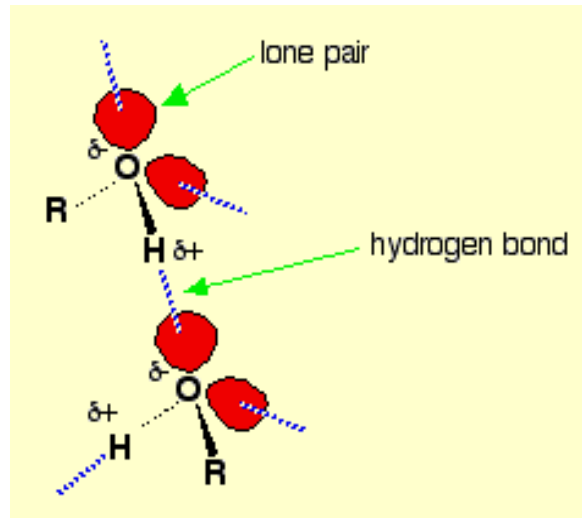
The patterns in boiling point reflect the patterns in intermolecular attractions.

# Properties of Alcohols

## Hydrogen bonding

Hydrogen bonding occurs between molecules where you have a hydrogen atom attached to one of the very electronegative elements - fluorine, oxygen or nitrogen.

In the case of alcohols, there are hydrogen bonds set up between the slightly positive hydrogen atoms and lone pairs on oxygens in other molecules.



The hydrogen atoms are slightly positive because the bonding electrons are pulled away from them towards the very electronegative oxygen atoms. In alkanes, the only intermolecular forces are van der Waals dispersion forces. Hydrogen bonds are much stronger than these and therefore it takes more energy to separate alcohol molecules than it does to separate alkane molecules.

That's the main reason that the boiling points are higher.

# Properties of Alcohols

## **The effect of van der Waals forces . . .**

. . . on the boiling points of the alcohols:

Hydrogen bonding isn't the only intermolecular force in alcohols. There are also van der Waals dispersion forces and dipole-dipole interactions.

The hydrogen bonding and the dipole-dipole interactions will be much the same for all the alcohols, but the dispersion forces will increase as the alcohols get bigger.

These attractions get stronger as the molecules get longer and have more electrons. That increases the sizes of the temporary dipoles that are set up.

This is why the boiling points increase as the number of carbon atoms in the chains increases. It takes more energy to overcome the dispersion forces, and so the boiling points rise.

# Properties of Alcohols

## **Solubility of alcohols in water**

The small alcohols are completely soluble in water. Whatever proportions you mix them in, you will get a single solution.

However, solubility falls as the length of the hydrocarbon chain in the alcohol increases. Once you get to four carbons and beyond, the fall in solubility is noticeable, and you may well end up with two layers in your test tube. The solubility of the small alcohols in water

Consider ethanol as a typical small alcohol. In both pure water and pure ethanol the main intermolecular attractions are hydrogen bonds. In order to mix the two, you would have to break the hydrogen bonds between the water molecules and the hydrogen bonds between the ethanol molecules. It needs energy to do both of these things.

However, when the molecules are mixed, new hydrogen bonds are made between water molecules and ethanol molecules. The energy released when these new hydrogen bonds are made more or less compensates for that needed to break the original ones. In addition, there is an increase in the disorder of the system - an increase in entropy. That is another factor in deciding whether things happen or not.

# Properties of Alcohols

## **The lower solubility of bigger alcohols**

Imagine what happens when you have got, say, 5 carbon atoms in each alcohol molecule.

The hydrocarbon chains are forcing their way between water molecules and so breaking hydrogen bonds between those water molecules.

The -OH end of the alcohol molecules can form new hydrogen bonds with water molecules, but the hydrocarbon "tail" doesn't form hydrogen bonds

That means that quite a lot of the original hydrogen bonds being broken aren't replaced by new ones.

All you get in place of those original hydrogen bonds are van der Waals dispersion forces between the water and the hydrocarbon "tails". These attractions are much weaker. That means that you don't get enough energy back to compensate for the hydrogen bonds being broken. Even allowing for the increase in disorder, the process becomes less feasible.

As the length of the alcohol increases, this situation just gets worse, and so the solubility falls.



# The Reaction of Alcohols

Due to the large difference in electronegativities all the reactions take place around the C-O-H group. It can react in two ways:

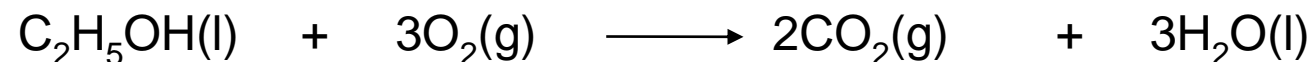
- The O-H bond breaks
- The C-O bond breaks – this is more common

In both of these cases the oxygen atom ends up with the negative charge because of its high electronegativity, it will always capture the electrons.

## Combustion

Alcohols burn completely with enough oxygen and incompletely if not enough oxygen is present.

Complete combustion:

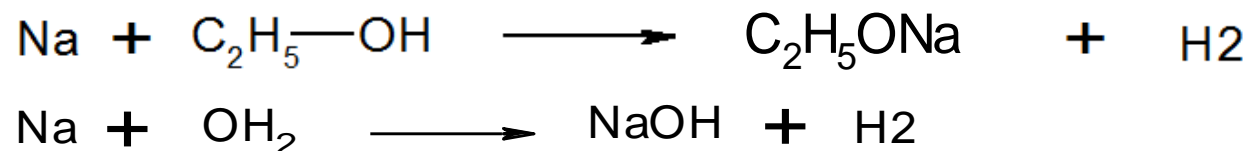


# Reactions of Alcohols

If a small piece of sodium is dropped into some ethanol, it reacts steadily to give off bubbles of hydrogen gas and leaves a colourless solution of sodium ethoxide,  $\text{CH}_3\text{CH}_2\text{ONa}$ . Sodium ethoxide is known as an alkoxide and is very alkaline.

If the solution is evaporated carefully to dryness, the sodium ethoxide is left as a white solid.

Compare this reaction to the reaction of sodium and water.



Sodium ethoxide is just like sodium hydroxide, except that the hydrogen has been replaced by an ethyl group. Sodium hydroxide contains  $\text{OH}^-$  ions; sodium ethoxide contains  $\text{CH}_3\text{CH}_2\text{O}^-$  ions.

Reaction of alcohols with sodium is a test for the  $-\text{OH}$  group. You would first need to make sure your solution is neutral (as reaction of sodium with acid is VERY violent). Assuming you do this and you drop a small piece of sodium into a water free, neutral solution and hydrogen gas is produced you know you have an alcohol.

# Reactions of Alcohols

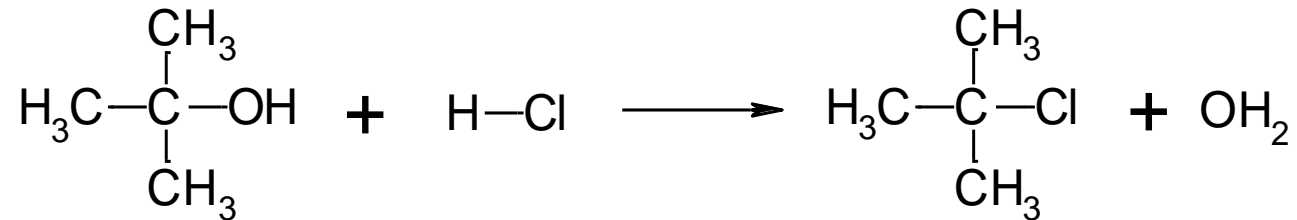
The general reaction looks like this:

Alcohols react with halogen halides (HCl, HBr, HI) to give halogenoalkanes. The rate of reaction is in the order  $\text{HI} > \text{HBr} > \text{HCl}$

## Making Chloroalkanes

It is possible to make tertiary chloroalkanes successfully from the corresponding alcohol and concentrated hydrochloric acid, but to make primary or secondary ones you really need to use a different method - the reaction rates are too slow.

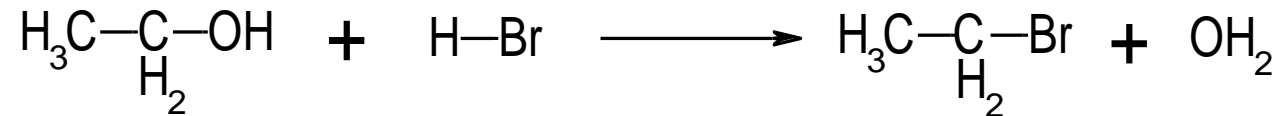
A tertiary chloroalkane can be made by shaking the corresponding alcohol with concentrated hydrochloric acid at room temperature.



# Reactions of Alcohols

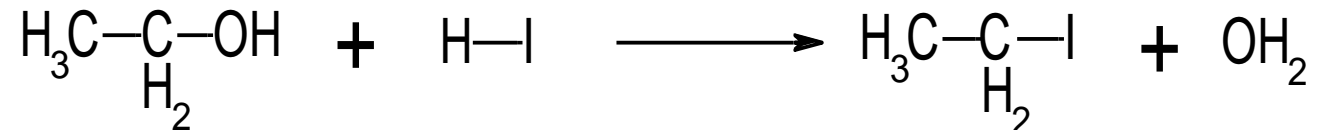
## Making bromoalkanes

Rather than using hydrobromic acid, you usually treat the alcohol with a mixture of sodium or potassium bromide and concentrated sulphuric acid. This produces hydrogen bromide which reacts with the alcohol.



## Making iodoalkanes

In this case the alcohol is reacted with a mixture of sodium or potassium iodide and concentrated phosphoric(V) acid,  $\text{H}_3\text{PO}_4$ , and the iodoalkane is distilled off. The mixture of the iodide and phosphoric(V) acid produces hydrogen iodide which reacts with the alcohol.

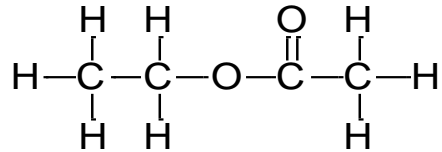


# Esters – Quick Summary

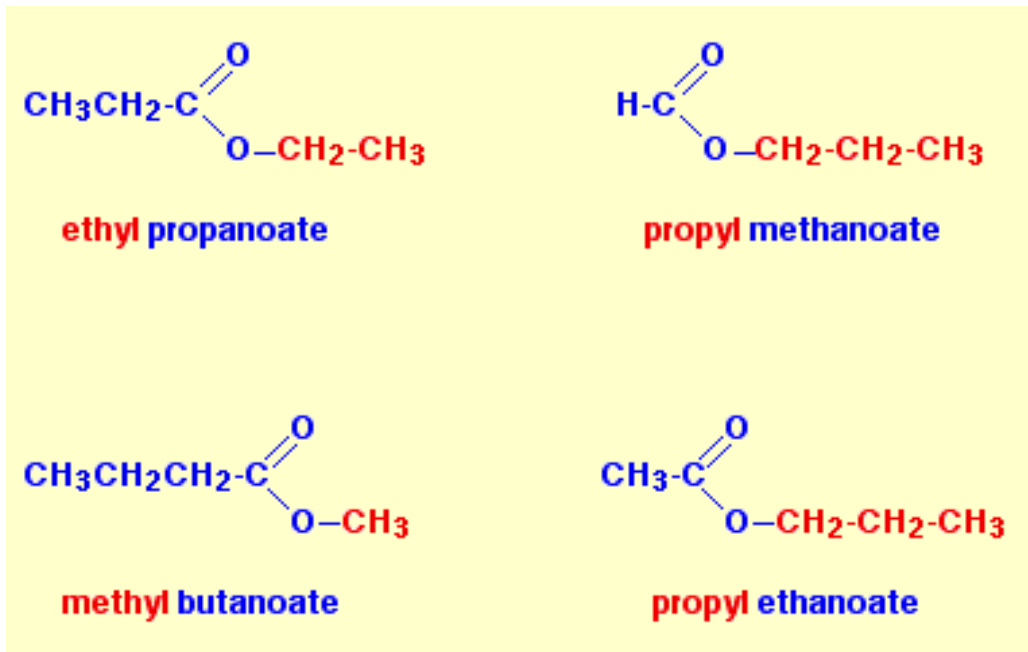
Esters are derived from carboxylic acids. A carboxylic acid contains the -COOH group, and in an ester the hydrogen in this group is replaced by a hydrocarbon group of some kind. We shall just be looking at cases where it is replaced by an alkyl group, but it could equally well be an aryl group (one based on a benzene ring).

A common ester - ethyl ethanoate

The most commonly discussed ester is ethyl ethanoate. In this case, the hydrogen in the -COOH group has been replaced by an ethyl group. The formula for ethyl ethanoate is:

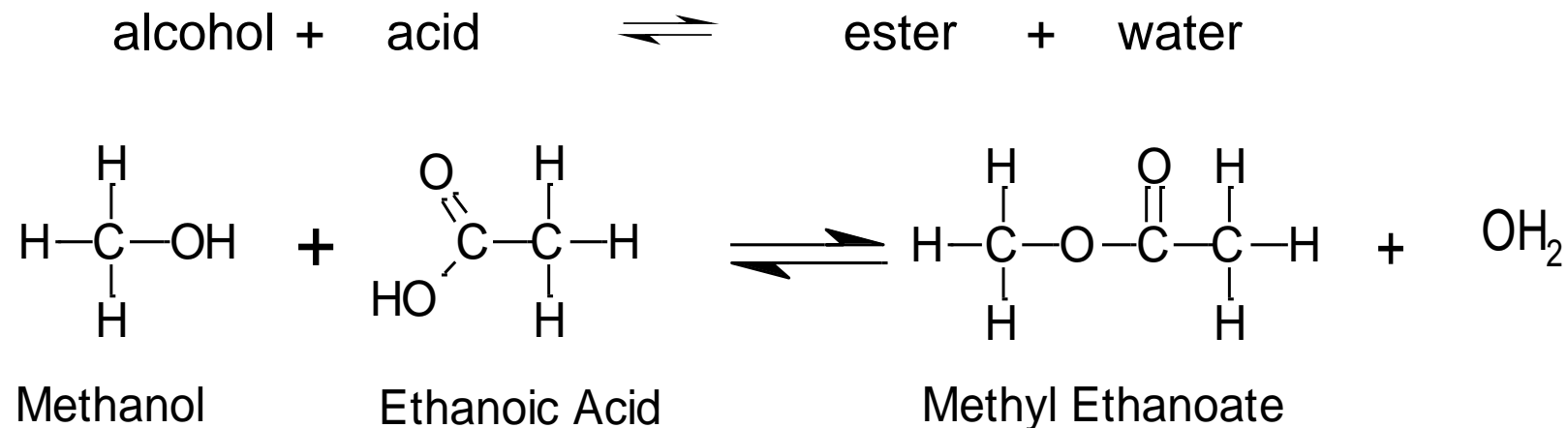


Here's the name of a few more esters.



# Esterification

Alcohols react with carboxylic acids (RCOOH), and a molecule of water is lost and an ester (RCOOR) is made. The general formula is:



This reaction is catalysed by strong acids, such as sulphuric acid. It is a reversible reaction and ends up at equilibrium with a mixture of reactants and products. Luckily enough you do not need to know the mechanism of this as it is very complex.

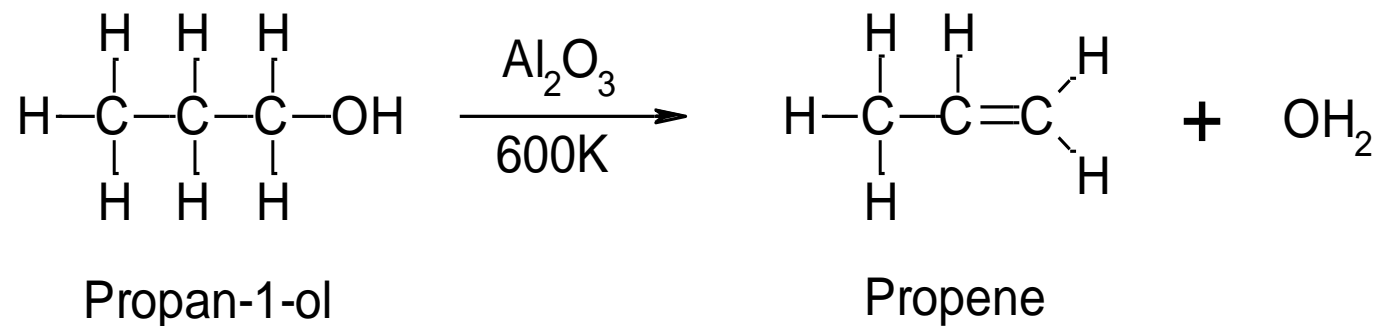
Smaller esters tend to smell like most organic solvents (that gluey smell) though larger esters have the smell of “pear drops”.

# Elimination/Dehydration reactions

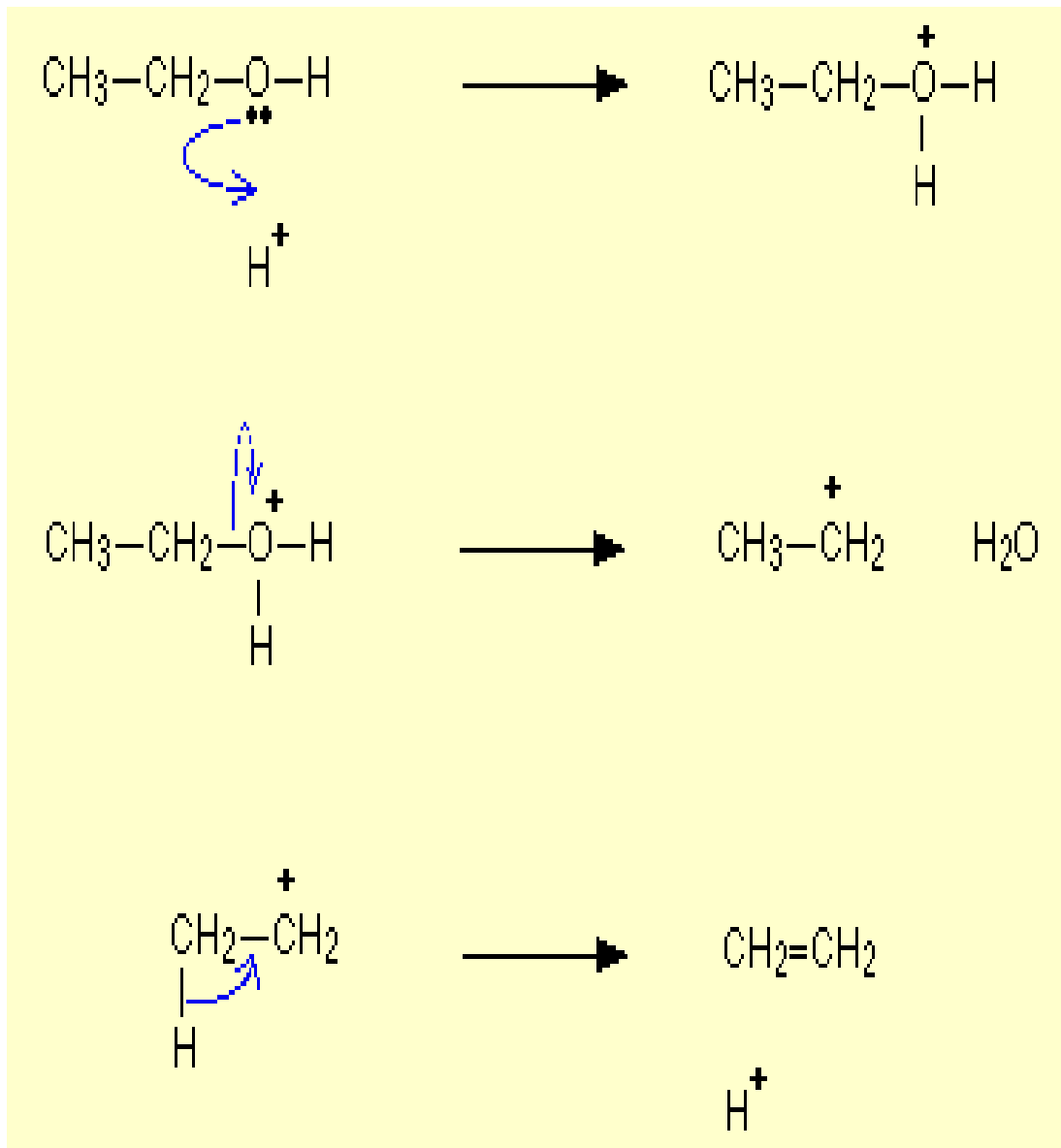
Elimination reactions are ones in which small molecules leave the parent molecule. For alcohols, this molecule is always water. This is from the OH group and a hydrogen molecule from the carbon next to the OH group.

So elimination reactions for alcohols are always dehydration reactions.

Alcohols can be dehydrated with hot concentrated sulphuric acid or by their vapours passing over an aluminium oxide catalyst. An alkene is then formed.



# Dehydration Mechanism



The oxygen atom in the ethanol has two active lone pairs of electrons, and one of these picks up a hydrogen ion from the sulphuric acid. The alcohol is said to be protonated.

In the second stage of the reaction the protonated ethanol loses a water molecule to leave a carbocation.

The hydrogen ion is pulled off by a hydrogensulphate ion to regenerate the sulphuric acid catalyst.



# Selective Oxidation Summary

Complete oxidation of alcohols is combustion – but this can be done more gently and in stages.

Primary alcohols are oxidised to aldehydes  $RCHO$ , and these can be further oxidised to carboxylic acids,  $RCOOH$ .

Secondary alcohols can be oxidised to ketones,  $R_2CO$  but cannot be further oxidised.

Tertiary alcohols cannot be oxidised by this method as this would need a C - C bond to break rather than a C - H bond in the previous examples, this is the reason ketones are not oxidised further.

To carry out selective oxidation, an acidified solution of potassium dichromate is used as the oxidising agent. In the reaction the dichromate ions go from the orange dichromate (VI) ions to the reduced green chromium (III) ions.