Organic chemistry – crib sheet

Ethers and esters

General

Ethers and esters are two groups very closely related to each other but with greatly different properties.

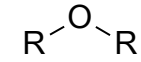
Ethers are very volatile (they change from liquid to gas at or close to room temperature) and are commonly used as anaesthetics (they have a low toxicity and are removed from the body rapidly)

Esters are more commonly used as parts of flavourings in the likes of crisps or as scents in perfumes. Like ethers, they evaporate at relatively low temperatures as neither ethers or esters have any hydrogens available for hydrogen bonding.

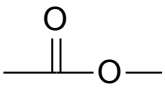
Structure and bonding

Ethers are formed by the reaction with metal alkoxide (formed by reacting an alcohol with Na^+) and a monohalogenated alkane. This formation works for both symmetrical (both the alcohol and alkane have the same number of carbons) or asymmetrical (the two compounds have different numbers of carbons in the chain).

This forms a carbon-oxygen-carbon bridge (*right*). Oxygen has a lone pair of electrons which makes it vulnerable to breakage by electrophilic attack. The oxygen tries to stabilise itself by drawing “electron density” from the neighbouring carbons resulting in the carbons being slightly electro-positive.



Ethers do not hydrogen bond to themselves, but may to water (as with other carbonyls, the degree of solubility depends on the alkyl chain length; the longer it is, the less soluble it is). They make good solvents as they are fairly unreactive and with the slight polarity, are able to dissolve both polar and non-polar molecules.



Esters (*left*) also have the same carbon-oxygen-carbon bridge, but on the carbon joining the bridge, have a double bonded oxygen. As with ethers, they do not hydrogen bond to themselves, but will to water.

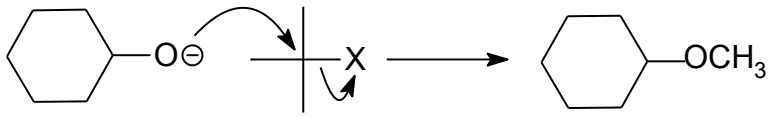
Esters also have a smell (scent) which gives them a wide range of uses from cosmetics to food additives (small esters easily evaporate at room temperatures). The low toxicity of esters also makes them safe for child products and food flavours.

Naming ethers

Ethers are formed from the reaction of an alcohol and monohalogenated alkane, so their name will come from a mixture of both (this is seen quite frequently in organic chemistry). With ethers though, it can be confusing!

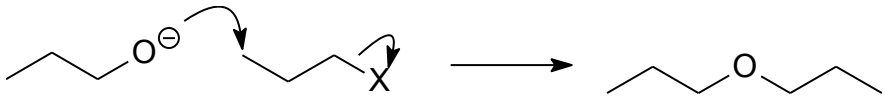
If the ether is unsymmetrical (the alkane and alcohol do not have the same number of carbons on them, which is quite frequently the case), the longer alkyl group gives the base name with the alcohol giving the group (add -oxy after the group e.g. methanol would give methoxy). If the alcohol has more carbons, the alkane becomes the group.

e.g.



The alkoxide of cyclohexanol reacts with a monohalogenated alkane. This is an unsymmetrical addition (cyclohexanol has more carbons than the alkane). As the alcohol has the larger number of carbons, the small alkane forms the group.

The alkane has one carbon, therefore has the skeletal name of meth. It is part of the ether, therefore has the ending -oxy (it becomes a methoxy group). The group part is added to the cycloalkane to give a full name of methoxycyclohexane.



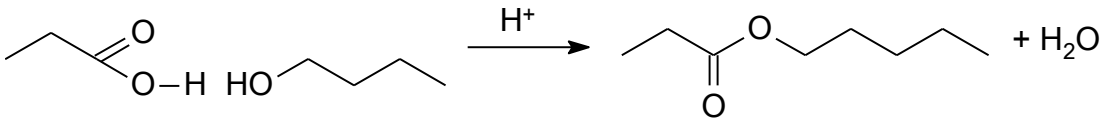
Here the carbonyls have the same number of carbons, they are symmetrical. It doesn't matter if the alcohol or the monohalogenated alkane take the oxy grouping. There are 3 carbons either side of the oxygen (skeletal name *prop*) which gives the name propoxypropane.

Naming esters

Esters, like ethers, come from two different molecules; a carboxylic acid and an alcohol using an acid catalyst to speed the reaction up.

Naming them is simple. The alcohol becomes the group (eg ethanol is ethyl). The acid part changes its end to -oate (eg ethanoic acid becomes ethanoate. This second part is known as the tail). The name is then just put together group-tail.

e.g.



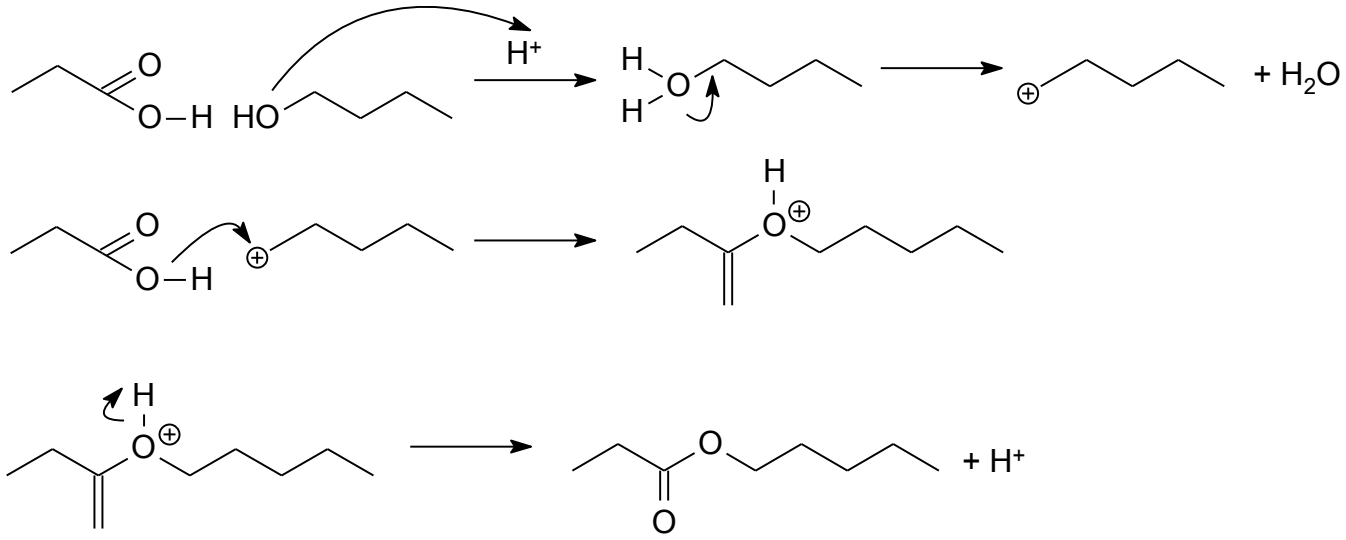
The acid here is propanoic acid and the alcohol is pentan-1-ol.

The pentan-1-ol becomes pentyl (the alcohol is normally a primary alcohol – secondary alcohols are less reactive and don't normally form esters though they can under some conditions).

Ethanoic acid drops the “oic acid” part and replaces it with “oate”

The name is therefore pentyl ethanoate.

The mechanism for the production of an ester is this



The first step is the hydrolysis of the alcohol to form the positively charged intermediate. This then breaks off to give a carbocation and water.

The charge on the oxygen lone pair is attracted to the newly formed carbocation and a new intermediate is formed. This intermediate is electronically unstable and quickly breaks down, releasing H^+ and forming the ester.

Uses of ethers

Ethers are typically used as solvents and “carriers”. They have a low toxicity and due to their low reactivity, are fairly inert. Small molecular weight ethers are normally used as carrier gases for anaesthetics (such as the halothane group of compounds) as they change from liquid to gas below that of the temperature of the body and are easily removed from the blood and lungs by simply removing the source of the gas.

Ethers are able to dissolve both polar and non-polar materials (polar due to the slight charge on the oxygen, non-polar due to the uncharged hydrocarbon groups on either side)

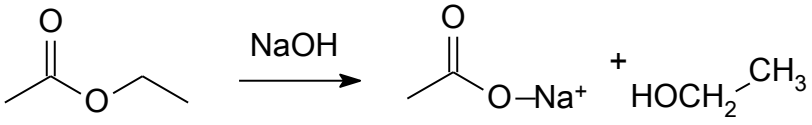
Uses of esters

Esters are widely used for flavourings. They occur naturally in fruits and flowers (for example, ethyl methanoate is found in raspberries and ethyl butanoate in pineapples).

Due to their volatility, esters are also good as drying agents in adhesives.

One of the main uses for esters is in the production of soap (the process is called saponification). Saponification is the reaction of an ester with a group I hydroxide (such as NaOH).

The ester reacts with the base to form the salt of the acid with alcohol also released.



Soaps have two ends – a hydrophobic (water hating) tail (these are from the carbon chain) and the positive hydrophilic (water loving) head.

Oils on the skin trap dirt and also help protect against infections from bacteria. They are long chain alkanes, so are not soluble in water. To remove the oils, the oil must first be dissolved in a non-polar solvent. However a non-polar solvent will not mix with water from the tap.

Soaps have a positively charged head which will be attracted to the water. The skin oil is mixed with the hydrocarbon chain of the soap. The head then pulls the tail into the water, so removing the oil from the skin. The oily end will still not mix with water, but will form an emulsion which is then rinsed down the sink.