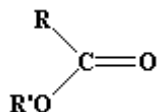


ESTERS

Esters are derivatives of the carboxylic acids in which the -OH part of the carboxylic group has been replaced by -OR group where R may be alkyl or aryl group.

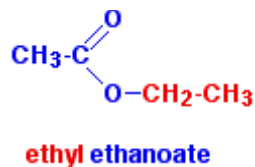
A carboxylic acid contains the -COOH group, and in an ester the hydrogen in this group is replaced by a hydrocarbon group of some kind. This could be an alkyl group like methyl or ethyl, or one containing a benzene ring like phenyl.

Esters are compounds formed from the reaction between alcohols and acids. The word 'ester' alone now signifies by common usage that the acid is an organic acid, but inorganic acids can also form esters - ATP is an example well-known to biology students, being a phosphate ester. Even halogenoalkanes can be regarded as inorganic esters, of alcohols and hydrochloric acid. This section is, however, confined to esters of organic acids RCOOR' where R can be hydrogen or an organic group:



A common ester - ethyl ethanoate

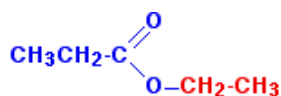
The most commonly discussed ester is ethyl ethanoate. In this case, the hydrogen in the -COOH group has been replaced by an ethyl group. The formula for ethyl ethanoate is:



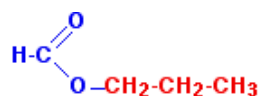
Notice that the ester is named the opposite way around from the way the formula is written. The "ethanoate" bit comes from ethanoic acid. The "ethyl" bit comes from the ethyl group on the end.

A few more esters

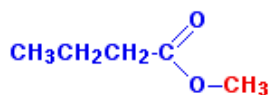
In each case, be sure that you can see how the names and formulae relate to each other.



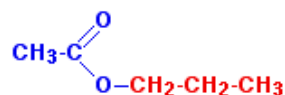
ethyl propanoate



propyl methanoate



methyl butanoate

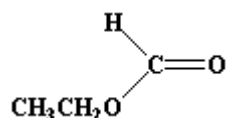


propyl ethanoate

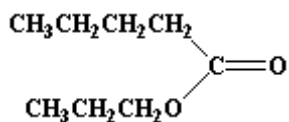
Notice that the acid is named by counting up the total number of carbon atoms in the chain - including the one in the -COOH group. So, for example, $\text{CH}_3\text{CH}_2\text{COOH}$ is propanoic acid, and $\text{CH}_3\text{CH}_2\text{COO}$ is the propanoate group.

Esters in the food industry

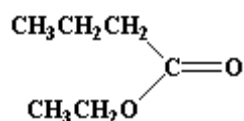
Esters are widely used for flavourings; many are 'nature-identical', that is synthetic versions of the esters present in the fruit. Fruit flavours are very complex, though, often arising from many different compounds, some of which are present in small quantities.



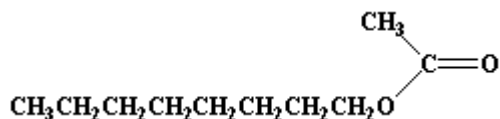
Ethyl methanoate (ethyl formate): rum flavouring



Propyl pentanoate (*n*-propyl *n*-valerate): pineapple flavouring



Ethyl butanoate (ethyl butyrate): apple odour



Octyl ethanoate (*n*-octyl acetate): orange odour

Physical properties

- Esters are usually colorless, neutral liquids, pleasant-smelling and generally insoluble in water but readily soluble in organic solvents.
- Many esters have a fruity odor and are prepared synthetically in large quantities for commercial use as artificial fruit essences and other flavorings and as components of perfumes.

MAKING ESTERS

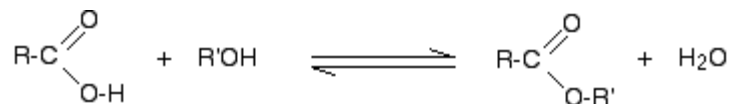
This page describes ways of making esters in the lab from alcohols and phenols using carboxylic acids, acyl chlorides (acid chlorides) or acid anhydrides as appropriate.

Making esters using carboxylic acids

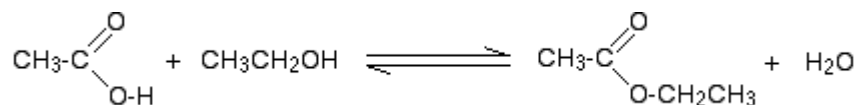
This method can be used for converting alcohols into esters, but it doesn't work with phenols - compounds where the -OH group is attached directly to a benzene ring. Phenols react with carboxylic acids so slowly that the reaction is unusable for preparation purposes.

The chemistry of the reaction

Esters are produced when carboxylic acids are heated with alcohols in the presence of an acid catalyst. The catalyst is usually concentrated sulphuric acid. Dry hydrogen chloride gas is used in some cases, but these tend to involve aromatic esters (ones where the carboxylic acid contains a benzene ring). The esterification reaction is both slow and reversible. The equation for the reaction between an acid RCOOH and an alcohol R'OH (where R and R' can be the same or different) is:



So, for example, if you were making ethyl ethanoate from ethanoic acid and ethanol, the equation would be:



Doing the reactions

On a test tube scale

Carboxylic acids and alcohols are often warmed together in the presence of a few drops of concentrated sulphuric acid in order to observe the smell of the esters formed.

You would normally use small quantities of everything heated in a test tube stood in a hot water bath for a couple of minutes.

Because the reactions are slow and reversible, you don't get a lot of ester produced in this time. The smell is often masked or distorted by the smell of the carboxylic acid. A simple way of detecting the smell of the ester is to pour the mixture into some water in a small beaker.

Apart from the very small ones, esters are fairly insoluble in water and tend to form a thin layer on the surface. Excess acid and alcohol both dissolve and are tucked safely away under the ester layer.

Small esters like ethyl ethanoate smell like typical organic solvents (ethyl ethanoate is a common solvent in, for example, glues).

As the esters get bigger, the smells tend towards artificial fruit flavouring - "pear drops", for example.

On a larger scale

If you want to make a reasonably large sample of an ester, the method used depends to some extent on the size of the ester. Small esters are formed faster than bigger ones.

To make a small ester like ethyl ethanoate, you can gently heat a mixture of ethanoic acid and ethanol in the presence of concentrated sulphuric acid, and distil off the ester as soon as it is formed.

This prevents the reverse reaction happening. It works well because the ester has the lowest boiling point of anything present. The ester is the only thing in the mixture which doesn't form hydrogen bonds, and so it has the weakest intermolecular forces.

Larger esters tend to form more slowly. In these cases, it may be necessary to heat the reaction mixture under reflux for some time to produce an equilibrium mixture. The ester can be separated from the carboxylic acid, alcohol, water and sulphuric acid in the mixture by fractional distillation.

Preparing Ester in the Lab

Procedure:

1. Place 25 mmol of the carboxylic acid and 12.5 mmol of the alcohol in a 5-mL conical vial containing a spin vane.
2. Add 8-10 drops of concentrated sulfuric acid. Place a water-jacketed reflux condenser on the 5-mL conical vial.
3. Start the water flowing through the condenser (water in the bottom, out the top) and begin heating the solution on a sand bath with stirring.
4. Heat the solution to boiling and reflux for 30 min.
5. After the reflux period, cool the solution in an ice bath. Once the solution has cooled, remove the water condenser and transfer the solution to a centrifuge tube.
6. Add 2 mL of cold water and 2 mL of diethyl ether to the solution. Cap the tube and gently shake, with frequent venting, to mix the layers.
7. Allow the layers to separate. Remove the aqueous layer and place it into a small flask.
8. To the organic layer in the centrifuge tube, add 1 mL of 5% sodium bicarbonate and swirl gently.
9. Once all gas evolution has ceased, cap the vial and shake with venting. Allow the layers to separate and transfer the aqueous layer to the flask containing the previous aqueous layer.

10. Repeat the extraction process with another 1 mL of 5% sodium bicarbonate.
11. Using litmus paper, check the pH of the combined aqueous layers. If the aqueous layer is still acidic, continue to extract with additional 1 mL portions of 5% sodium bicarbonate until the combined aqueous layer is no longer acidic.
12. Dry the organic layer by adding a small amount of anhydrous sodium sulfate.
13. Use a filter pipet (pipet containing a small plug of cotton) to transfer the dried organic solution into a pre weighed conical vial.
14. Remove the solvent (diethyl ether) using a warm sand bath IN THE HOOD. Once the solvent is removed, weigh the vial and determine the yield of the crude ester.

Conclusion:

This experiment revealed the fragrant aromas that some esters can have. But esters also play an important role in biological processes as well as in medical applications. List at least one biological and one medical application in which esters play an important role.

Reaction of Esters

Hydrolysing Esters

This page describes ways of hydrolysing esters - splitting them into carboxylic acids (or their salts) and alcohols by the action of water, dilute acid or dilute alkali. It starts by looking at the hydrolysis of simple esters like ethyl ethanoate, and goes on to look at hydrolysing bigger, more complicated ones to make soap.

Hydrolysing simple esters

Technically, hydrolysis is a reaction with water. That is exactly what happens when esters are hydrolysed by water or by dilute acids such as dilute hydrochloric acid.

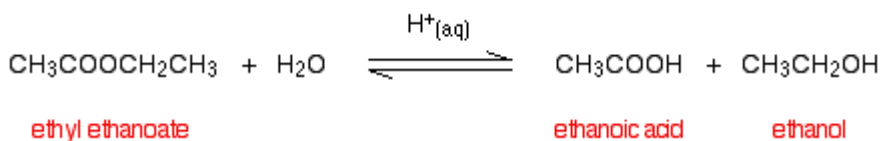
The alkaline hydrolysis of esters actually involves reaction with hydroxide ions, but the overall result is so similar that it is lumped together with the other two.

Hydrolysis using water or dilute acid

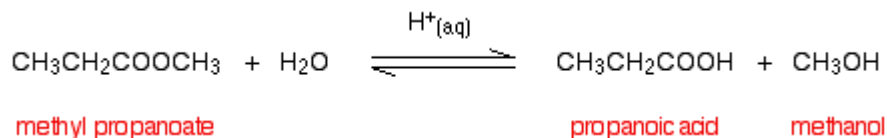
The reaction with pure water is so slow that it is never used. The reaction is catalysed by dilute acid, and so the ester is heated under reflux with a dilute acid like dilute hydrochloric acid or dilute sulphuric acid.

Here are two simple examples of hydrolysis using an acid catalyst.

First, hydrolysing ethyl ethanoate:



. . . and then hydrolysing methyl propanoate:



Notice that the reactions are reversible. To make the hydrolysis as complete as possible, you would have to use an excess of water. The water comes from the dilute acid, and so you would mix the ester with an excess of dilute acid.

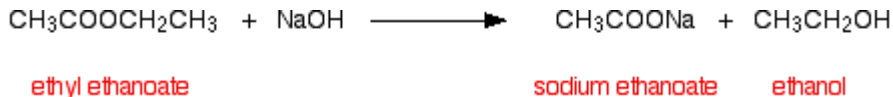
Hydrolysis using dilute alkali

This is the usual way of hydrolysing esters. The ester is heated under reflux with a dilute alkali like sodium hydroxide solution.

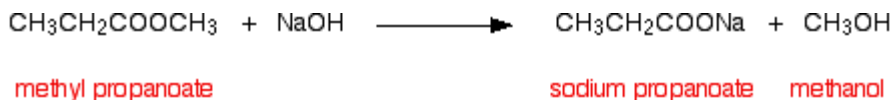
There are two big advantages of doing this rather than using a dilute acid. The reactions are one-way rather than reversible, and the products are easier to separate.

Taking the same esters as above, but using sodium hydroxide solution rather than a dilute acid:

First, hydrolysing ethyl ethanoate using sodium hydroxide solution:



. . . and then hydrolysing methyl propanoate in the same way:



Notice that you get the sodium salt formed rather than the carboxylic acid itself.

This mixture is relatively easy to separate. Provided you use an excess of sodium hydroxide solution, there won't be any ester left - so you don't have to worry about that.

The alcohol formed can be distilled off.

If you want the acid rather than its salt, all you have to do is to add an excess of a strong acid like dilute hydrochloric acid or dilute sulphuric acid to the solution left after the first distillation.

If you do this, the mixture is flooded with hydrogen ions. These are picked up by the ethanoate ions (or propanoate ions or whatever) present in the salts to make ethanoic acid (or propanoic acid, etc). Because these are weak acids, once they combine with the hydrogen ions, they tend to stay combined.

The carboxylic acid can now be distilled off.

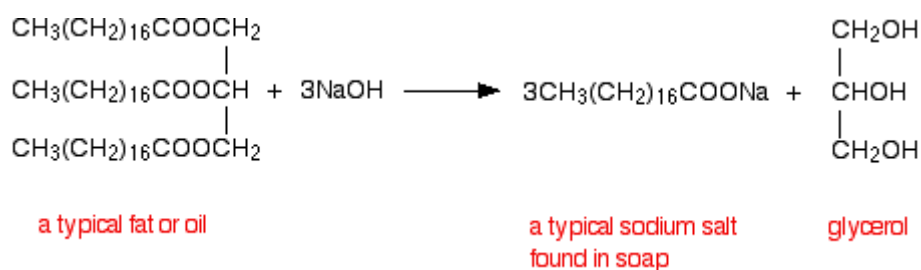
Hydrolysing complicated esters to make soap

This next bit deals with the alkaline hydrolysis (using sodium hydroxide solution) of the big esters found in animal and vegetable fats and oils.

If the large esters present in animal or vegetable fats and oils are heated with concentrated sodium hydroxide solution exactly the same reaction happens as with the simple esters.

A salt of a carboxylic acid is formed - in this case, the sodium salt of a big acid such as octadecanoic acid (stearic acid). These salts are the important ingredients of soap - the ones that do the cleaning.

An alcohol is also produced - in this case, the more complicated alcohol, propane-1,2,3-triol (glycerol).



Because of its relationship with soap making, the alkaline hydrolysis of esters is sometimes known as **saponification**. (Refer to topic 12)

Uses of Esters

Esters are used as softeners in molding and plastic industries, in artificial fragrances or scents, as solvents in pharmaceutical industries, as industrial solvents for making fats, cellulose, paints and varnishes, and used in making artificial food flavors that are added into food such as ice cream and sweets.

Examples:

a) **Methyl Salicylate** (or *Oil of Wintergreen*) has the chemical formula C₈H₈O₃. It is prepared mostly by esterification of salicylic acid with methanol and is present naturally in the leaves of *Gaultheria procumbens* and in the bark of *Betula lenta*. Methyl Salicylate is used in perfumery and for flavouring sweets, as well as a therapeutic use as a counter-irritant.

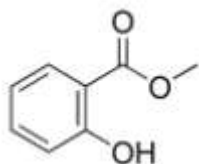
b) **Ethyl Acetate** (or *Acetic Acid Ethyl Ester*, or *Vinegar Naphtha*) has the chemical formula C₄H₈O₂, and is obtained by slow distillation of a mixture of acetic acid, ethyl alcohol and

sulfuric acid. Its uses are varied, and include a pharmaceutical aid (flavour); artificial fruit essences; solvent for nitrocellulose, varnishes, lacquers and aeroplane dopes; cleaning textiles, and more!

c) **Ethyle Acrylate** (or *Acrylic Acid Ethyl Ester*) has the chemical formula $C_5H_8O_2$, and is prepared from ethylene chlorohydrin or acrylonitrile, ethanol, and sulfuric acid; also by an oxo reaction from acetylene, carbon monoxide and ethanol in the presence of suitable catalysts. Ethyl Acrylate is used as a monomer in the manufacture of water emulsion paint vehicles, in the production of emulsion-based polymers used in textile and paper coatings, leather finish resins and adhesives, and imparts flexibility to hard films.

Uses of Esters

- Esters are used in making various products like plastics, polymers, explosives.
- They are also used as solvent for oils, fats, cellulose resins etc.,
- They are also used in making artificial flavours and essences.
- Esters are also being successively used as the alternative to diesel.
- The salicylic methylester has amazing fragrance, the formula is given below.



AMIDES

Acid amides may be regarded as the derivatives of carboxylic acids in which -OH part of the carboxylic group is replaced by the -NH₂ group.

Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from the two molecules of the acid.

MAKING AMIDES

This page describes the preparation of amides from carboxylic acids, acyl chlorides (acid chlorides) and acid anhydrides.

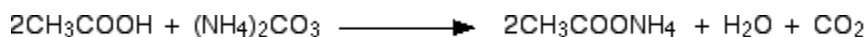
Making amides from carboxylic acids

Summary of the process

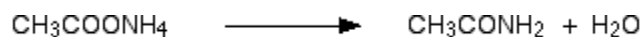
The carboxylic acid is first converted into an ammonium salt which then produces an amide on heating.

The ammonium salt is formed by adding solid ammonium carbonate to an excess of the acid.

For example, ammonium ethanoate is made by adding ammonium carbonate to an excess of ethanoic acid.



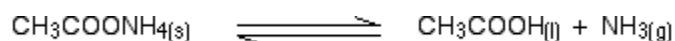
When the reaction is complete, the mixture is heated and the ammonium salt dehydrates producing ethanamide.



The excess of ethanoic acid is there to prevent dissociation of the ammonium salt before it dehydrates.

Ammonium salts tend to split into ammonia and the parent acid on heating, recombining on cooling. If dissociation happened in this case, the ammonia would escape from the reaction mixture and be lost. You couldn't get any recombination.

The dissociation is reversible:



The presence of the excess ethanoic acid helps to prevent this from happening by moving the position of equilibrium to the left.

Some brief practical details

The ammonium carbonate is added slowly to concentrated ethanoic acid and the reaction is left until all production of carbon dioxide stops.

It is then heated under reflux for half an hour for the dehydration to take place.

The mixture is distilled at about 170°C to remove excess ethanoic acid and water - leaving almost pure ethanamide in the flask.

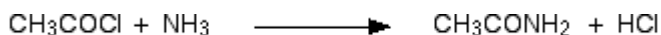
Making amides from acyl chlorides

Acyl chlorides (also known as acid chlorides) have the general formula RCOCl. The chlorine atom is very easily replaced by other things. For example, it is easily replaced by an -NH₂ group to make an amide.

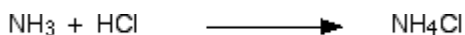
To make ethanamide from ethanoyl chloride, you normally add the ethanoyl chloride to a concentrated solution of ammonia in water. There is a very violent reaction producing lots of white smoke - a mixture of solid ammonium chloride and ethanamide. Some of the mixture remains dissolved in water as a colourless solution.

You can think of the reaction as happening in two stages.

In the first stage, the ammonia reacts with the ethanoyl chloride to give ethanamide and hydrogen chloride gas.



Then the hydrogen chloride produced reacts with excess ammonia to give ammonium chloride.



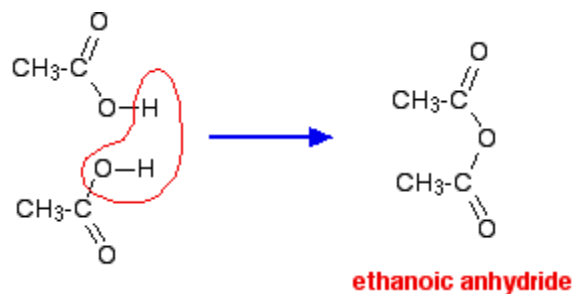
. . . and you can combine all this together to give one overall equation:



Making amides from acid anhydrides

An acid anhydride is what you get if you remove a molecule of water from two carboxylic acid - COOH groups.

For example, if you took two ethanoic acid molecules and removed a molecule of water between them you would get the acid anhydride, ethanoic anhydride (old name: acetic anhydride).



For equation purposes, ethanoic anhydride is often written as $(\text{CH}_3\text{CO})_2\text{O}$.

The reactions of acid anhydrides are rather like those of acyl chlorides except that during their reactions, a molecule of carboxylic acid is produced rather than the HCl formed when an acyl chloride reacts.

If ethanoic anhydride is added to concentrated ammonia solution, ethanamide is formed together with ammonium ethanoate. Again, the reaction happens in two stages.

In the first stage, ethanamide is formed together with ethanoic acid.



Then the ethanoic acid produced reacts with excess ammonia to give ammonium ethanoate.



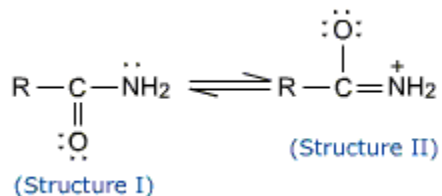
... and you can combine all this together to give one overall equation:



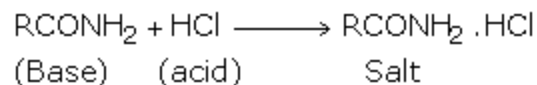
You need to follow this through really carefully, because the two products of the reaction overall can look confusingly similar.

Reaction of Amides

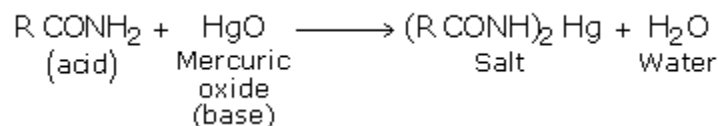
- (i) Amides are feeble bases. The lone pair of electrons on the nitrogen atom is responsible for the basic character. This lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group (structure II). Thus the electron pair of nitrogen is not easily available for protonation. Consequently the basic character is considerably decreased.



The basic character of the amide is illustrated in the following reaction with hydrochloric acid (an acid) to form a salt.

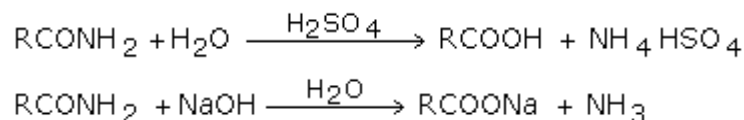


However, under suitable conditions, amides can also exhibit feeble acidic character. The amide (acting in the capacity of an acid) reacts with mercuric oxide (a base) to form mercury salt and water.

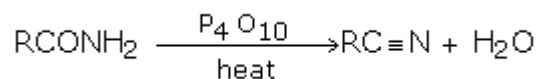


Thus amides are said to be amphoteric in nature as they exhibit both acidic and basic character.

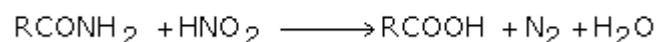
- (ii) Amides are hydrolyzed by aqueous solutions of mineral acids or alkalis to give carboxylic acids.



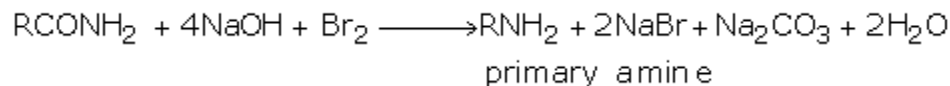
- (iii) Primary amides get dehydrated with phosphorous pentoxide to give nitriles.



- (iv) On treatment with nitrous acid, primary amides give carboxylic acid and nitrogen gas. The volume of nitrogen can be measured to determine the amide quantitatively.

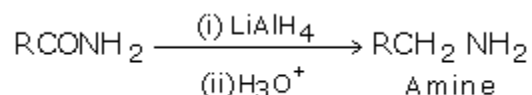


- (v) When primary amides are treated with bromine in the presence of an alkali, a primary amine containing one carbon less than the amide is formed.



The reaction involves molecular management in which alkyl or aryl group migrates from the acyl carbon to nitrogen. This reaction is known as Hofmann Bromamide reaction and is useful for descending of series i.e., preparing a lower homologue from a higher one.

- (vi) Amides are reduced to amines with LiAlH_4 .



Uses of Amides

- Amides are used widely in the as color, in crayons, pencils and inks, paper industry , plastic and rubber industry, and water and sewage treatment.
- Acryl amide and polyacrylamide are the most commonly used amides in these industries. But as, acrlamide is carcinogenic, it can be used only if the chemicals are not used for consumption. Polyacrylamide is used in its place, mainly for that reason, in the treatment of drinking water and sewage.
- Nylons are polyamides used for various purposes. Apart from textiles for clothing and carpets, nylon is also used to make tyre cords (the inner structure of a vehicle tyre which is underneath the rubber).The nylon fibres are also used to make ropes and nylon can be cast easily into solid shapes and used for cogs and bearings in machines.
- In paper industry polyacrylamide is used as a binder and for retention for fibres. It is also used to retain the color pigments on the paper.
- Polyacrylamide is used as a coating on many household appliances and car parts with thermosetting acrylics.
- Acrylamides are used in the cosmetic industry to prepare hair products, soaps, and pre-shave lotions. Acrylamides are also used for printing inks, explosives, latex thickeners, adhesives and emulsion stabilizers.
- Kevlar a form of polyamide is a very strong material which is about five times as strong as steel, weight for weight. It is used in composites for boat construction, in manufacture of bulletproof vests, and in lightweight mountaineering ropes and skis and racquets.
- Acetaminophen an amide is used as asanalgesic (pain-killer). It is used as active ingredient in products such as Amadil, Datriil, Cetadol, Naprinol, Tylenol, and Panadol. Another amide analgesic is phenacetin, used in products such as Empirin and APC (aspirin, phenacetin, and caffeine) tablets.
- Other commercially used amides includes N,N-dimethyl-m-toluamide, used as insect repellent), lidocaine (Xylocaine) and dibucaine (Nupercaine), used as the local anesthetics, the tranquilizer meprobromate (Equaine, Miltown), and Sevin and Mipcin used as insecticides.

References:

<http://www.chemguide.co.uk/organicprops/esters/background.html>

<http://www.chemguide.co.uk/organicprops/amides/preparation.html#top>

<http://www2.volstate.edu/msd/CHE/242/Labs/Ester.htm>

<http://www.tutorvista.com/chemistry/ester-group>