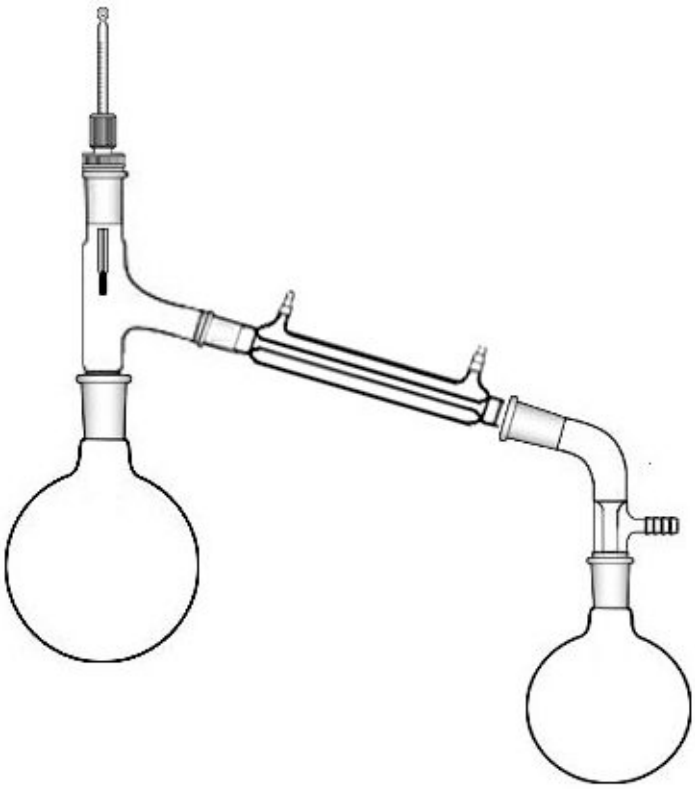
Kelso High School
Revised Advanced Higher

Practical Skills & Techniques



Book 2: Organic Techniques

Contents

Organic techniques

Introduction

Practical organic chemistry is primarily concerned with synthesising (making) organic compounds and the purpose of a '**synthesis**' is to prepare a **pure** sample of a specified compound. Essentially, there are five steps involved:

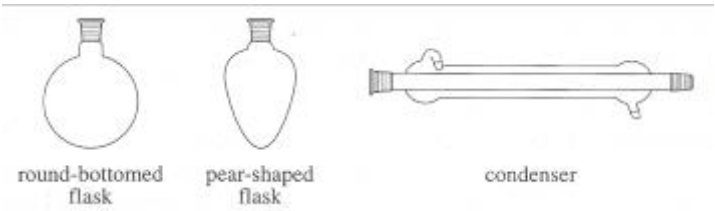
- **preparation** – the appropriate reaction is carried out and a crude sample of the desired product is prepared
- **isolation** – the crude sample of the product is separated from the reaction mixture
- **purification** – the crude product is purified
- **identification** – the identity of the pure compound is confirmed
- calculation of the **percentage yield**.

Apart from the last, each of the steps entails a variety of experimental techniques and operations, and in what follows some of the more important ones will be described. While they will be considered from a practical standpoint, we will touch on their theoretical basis where appropriate.

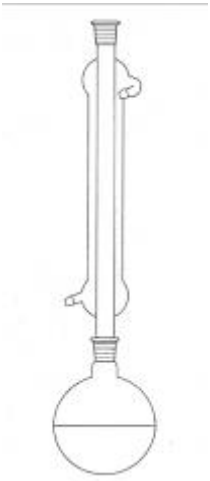
Preparation

Most organic preparations are carried out in fairly complex assemblies of glassware. The glassware has ground-glass joints that allow the individual pieces to fit together tightly, thus eliminating any need for corks or rubber stoppers.

Suppose we had to prepare a compound that required the reactants to be heated, which is generally the case in organic chemistry. Let's look at the glassware needed. It is illustrated below and consists of a round-bottomed or pear-shaped flask and a condenser.



The assembled apparatus is shown below with the condenser mounted vertically above the reaction flask. The reaction flask should be of a size such that when the reactants are in place it is about half full.



A **heating mantle** is generally used to heat the reactants. It has a cavity shaped to accommodate the reaction flask and has a variable regulator to control the rate of heating. While other heating devices, eg a hot-water bath, a steam bath, an oil bath or a sand bath, can be used, on no account should a reaction mixture be heated using a Bunsen burner. This is because organic compounds are generally flammable and if fires are to be prevented there must be no naked flames.

Once a reaction flask of the correct size has been selected, it is weighed empty and after adding the limiting reactant, ie the one that is not in excess, it is reweighed. During weighing, the flask can be supported on a cork ring to prevent it toppling over. We need to know the initial mass of the limiting reactant in order to calculate the theoretical yield and hence the percentage yield of product. The other reactants can now be added to the flask along with a few anti-bumping granules. If any of the reactants are solids or immiscible liquids, it may be necessary at this stage to add a solvent to give a homogeneous mixture. The apparatus is then assembled (see above) with the flask resting in a heating mantle. The rubber tubing attached to the lower end of the condenser should be connected to a cold-water tap and a steady flow of water is allowed to circulate. Before the heating mantle is switched on and the mixture gently heated, you should check that the flask and condenser are firmly clamped and the joint between them is tight.

As the reaction mixture heats up the more volatile components will boil and their vapours will rise into the condenser. There, they will be cooled, liquefied and returned to the reaction flask. The purpose of the condenser is to prevent the escape of any volatile reactants or products from the

apparatus. The operation of boiling a reaction mixture and condensing the vapours back into the reaction flask is known as **heating under reflux** or more commonly as **refluxing**.

When a reaction mixture is being heated, there is a tendency for it to boil violently as large bubbles of superheated vapour suddenly erupt from the mixture. This phenomenon is known as **bumping** and it can be prevented by the addition of a few **anti-bumping granules** (also called boiling stones) to the reaction mixture. They are normally made from pieces of alumina (aluminium oxide) or carborundum (silicon carbide) and have an air-filled porous surface that promotes the formation of a steady stream of tiny bubbles instead of a few large ones. Anti-bumping granules must always be added before heating begins because adding them to a hot mixture is likely to cause it to froth over. If the preparation requires the reaction mixture to be cooled and reheated, then fresh anti-bumping granules must be added before reheating commences. This is because when boiling stops, liquid is drawn into the pores of the granules and renders them ineffective.

Once the reaction is complete, the heating mantle is switched off and the reaction mixture is allowed to cool. During this time, the condenser must remain in place and the cold water must be kept circulating, otherwise the product may escape from the top of the condenser.

Sometimes, organic preparations require the addition of a reactant during the course of the reaction. If this is the case, then a two- or three-necked round-bottomed flask can be used, with the reactant being added from a dropping funnel placed in a side neck.

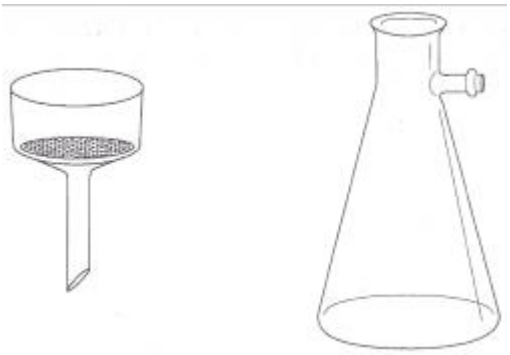
Isolation

After the preparation stage of a synthesis experiment has been completed, there will often be a bewildering mixture of substances in the reaction flask. Along with the desired product, the mixture is likely to contain:

- reactants that were used in excess
- other products of the reaction
- compounds that are produced as a result of side-reactions
- the limiting reactant if the reaction was a reversible one.

The next step in the overall process is to **isolate** or **separate** the compound we set out to prepare from the other components of the mixture. If the desired product is present as a **solid**, then **filtration** provides a fast and convenient way of separating it. This is normally carried out under reduced pressure, which is why the technique is often referred to as **vacuum filtration**. This type of filtration is performed with the aid of a Buchner funnel and flask or

Hirsch funnel and filter tube and which is used depends on the amount of solid to be filtered.



Buchner funnel and flask

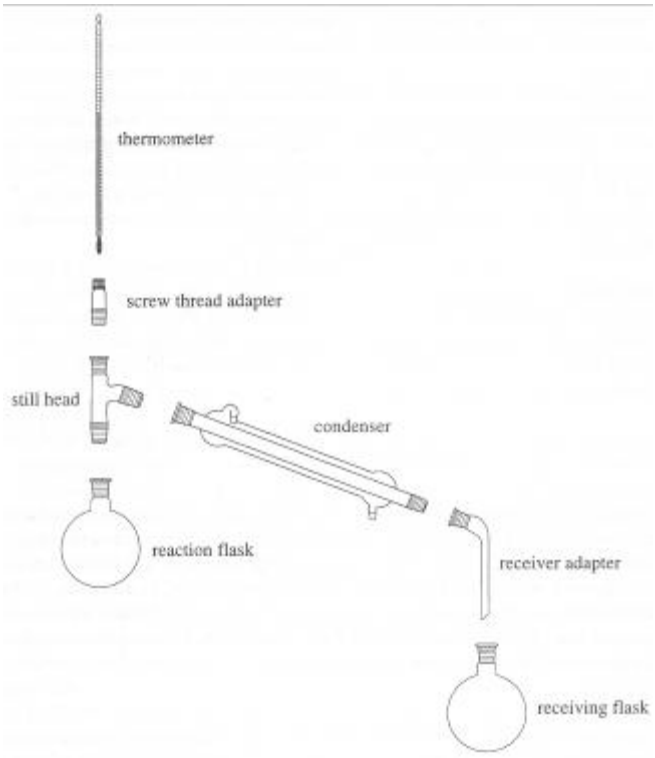
Hirsch funnel and filter tube

The Buchner and Hirsch funnels each have a plate incorporated in their base that is perforated by a number of small holes. The Buchner flask is simply a thick-walled conical flask with a short side arm and the Hirsch filter tube is a side-armed pyrex test-tube. The funnel is fitted into the neck of the flask or filter tube by means of a rubber stopper and the flask or filter tube is attached to a water pump via its side arm.

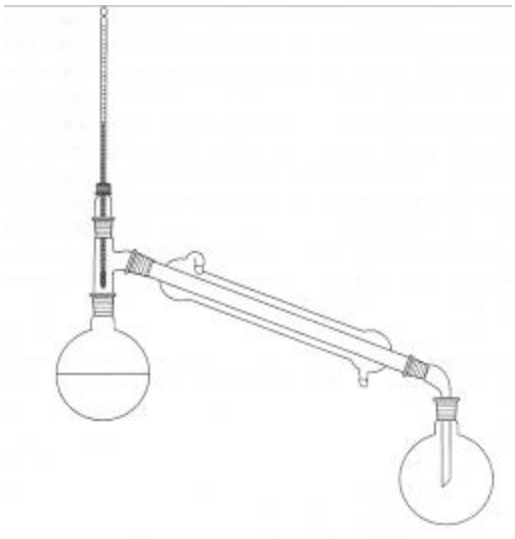
Before filtration, a filter paper is placed on the perforated plate – it should be of such a size that it sits flat on the plate and covers all the holes. The filter paper is moistened with a few drops of the liquid present in the mixture and the water pump is turned on. This ensures that the filter paper adheres firmly to the perforated plate and in the subsequent filtration will prevent any solid matter from passing round and under the edge of the paper into the flask. The mixture can now be filtered and it is added to the funnel in portions. If the solid is finely divided, then transfer of the bulk of the solid should be delayed to near the end of the filtration, otherwise the pores in the filter paper will become clogged and cause the rate of filtration to slow down.

Inevitably some of the solid product will remain in the reaction flask and if we are to gain maximum yield, it needs to be in the funnel. To do this, some of the filtrate is returned to the reaction flask and the mixture is stirred or swirled and quickly poured into the funnel. This operation is repeated until all the solid is transferred. The product is then washed with two or three portions of a suitable liquid to remove the bulk of the impurities adhering to its surface. You will be advised of a suitable liquid but obviously it must not dissolve the solid. To make it easier to handle, the product is partially dried by having air drawn through it for several minutes. The crude sample is then ready for purification.

If the desired product is present as a **liquid** in the reaction mixture and it is more volatile than the other substances in the mixture, then it is possible to isolate it by **simple distillation**. The individual items required for such an operation are illustrated and identified in the following diagram.



As in the preparation stage, the liquid mixture should occupy about half the volume of the round-bottomed distillation flask. The apparatus is then assembled as in the following diagram with the distillation flask sitting in a heating mantle and some fresh anti-bumping granules added to the mixture.

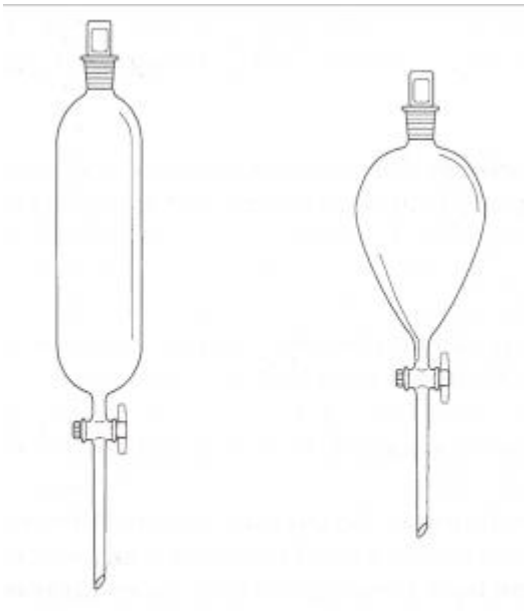


Notice that the receiver adapter does not fit tightly into the receiving flask, ie the latter is open to the atmosphere. For the accurate measurement of temperature, it is important that the thermometer is positioned correctly. It should be arranged such that the top of the bulb is level with the bottom of the still head's side arm. The rubber tubing on the lower end of the condenser is attached to the cold-water tap and water is allowed to circulate. Before heating commences, the apparatus must be checked to ensure that it is firmly clamped and that all the joints are tight apart from the point where the receiver adapter enters the receiving flask.

The heating mantle is switched on and the mixture is slowly distilled. Only the liquid that distils over within a certain temperature range should be collected in the receiving flask. The temperature range will be specified in the procedure but it will encompass the temperature at which the pure product boils. The range is also likely to be wide (20 °C or so) to make sure that the maximum amount of desired product is isolated from the mixture. If the liquid product is particularly volatile, it is good practice to place the receiving flask in an ice/water bath and to ensure the receiver adapter on the condenser extends well into the flask. Such measures ought to minimise loss of product through evaporation.

On occasions it may not be practicable to isolate the product directly from the mixture by filtration or simple distillation. In such cases we have to resort to another technique known as **solvent extraction**. Suppose, for example, our desired product is present in an aqueous mixture, ie water is the solvent. It can be removed or extracted from the mixture by the addition of a second solvent. The choice of the second solvent is critical. It must be **immiscible** with water, ie when the two are mixed they form separate layers. Furthermore, the product must not react with the solvent and it must be **more soluble** in it than in water. Hence, on adding the solvent to the aqueous mixture the product will move out of the aqueous layer and into the solvent layer, from which it can be more readily separated. The practical details of solvent extraction are outlined below.

The aqueous layer is first transferred to a **separating funnel**, which may be cylindrical or pear-shaped, as illustrated below.



A portion of solvent, equal to about one-third of the volume of the aqueous mixture, is then added to the funnel. For efficient extraction, the total volume of both liquids should not exceed three-quarters of the funnel's capacity. With the stopper held firmly in place, the funnel is inverted and the tap opened to release any pressure build-up caused by the solvent vaporising. The tap is then closed and the mixture is shaken for several minutes. This increases the surface area of contact between the two liquids and so speeds up the rate of movement of the product from the aqueous layer into the solvent layer. During the shaking process, it is important to invert the funnel from time to time and open the tap to release the pressure.

With the funnel supported, the mixture is allowed to settle until the layers have completely separated – there should be a sharp dividing line between the two. Let's assume that the aqueous layer is more dense than the solvent layer, in which case the solvent layer will lie above the aqueous layer. With the stopper removed, the lower aqueous layer is drained through the tap into a conical flask. The solvent layer is poured out of the top of the funnel into a separate flask. This avoids contamination with any drops of the aqueous mixture remaining in the stem of the funnel. The aqueous layer is then returned to the separating funnel and the above procedure is repeated at least twice using a fresh portion of solvent each time. The reason why several extractions are carried out using small volumes of solvent rather than one extraction using a large volume of solvent is that a greater amount of product can be recovered in this way, ie the extraction process is more efficient.

The solvent extracts are then combined and the solvent is removed by careful distillation, leaving the desired product in the distillation flask.

Purification

No matter whether the product was isolated from the reaction mixture by filtration, simple distillation or solvent extraction, it is highly unlikely that the separation would be 'clean'. In other words, impurities will still be present and these require to be removed from the sample.

The method used to purify the product sample depends on its state, ie whether it is a solid or a liquid. The simplest and most widely used technique of purifying an organic **solid** is **recrystallisation**. In a typical recrystallisation procedure, the crude or impure solid is dissolved, by heating, in the minimum volume of a suitable solvent. The hot saturated solution that is formed is filtered and allowed to cool, whereupon the solid crystallises out. The crop of pure crystals can then be filtered off, leaving the bulk of the soluble impurities in the filtrate or **mother-liquor** as it is more often called.

The success of the recrystallisation process depends largely on the choice of solvent. First and foremost, the substance to be purified must not react with the solvent. In addition, it should have a high solubility in the hot solvent and be virtually insoluble in the cold solvent. Ideally, the impurities should be completely insoluble in the hot solvent, in which case they will be removed when the hot solution is filtered or completely soluble in the cold solvent so that they remain in the mother-liquor and can be separated from the pure solid in the second filtration. However, finding a solvent that meets these requirements is a long, laborious process. Fortunately, at this stage in your career, you will be spared this since in the experiments you tackle, the preferred recrystallisation solvent will be specified.

Let's now consider the practical aspects of recrystallisation. The detailed procedure is outlined below.

The crude solid is carefully transferred to a clean conical flask. A small volume of solvent – sufficient to just cover the solid – is added together with a couple of anti-bumping granules. The flask should then be placed on a hot plate and the mixture gently heated until it boils. A hot plate is used since the solvent is likely to be flammable. If the solid hasn't all dissolved, then a little more solvent should be added and the mixture heated to boiling once again. This process is repeated until all the solid dissolves and then a little excess solvent is added to keep it in solution. Some impurities may be completely insoluble and so care must be taken not to add too much solvent in attempting to dissolve them. The next stage in the process is to filter the hot solution through a **'fluted' filter paper**, supported in a glass filter funnel, into a

second conical flask. This removes insoluble material – things like dust particles, anti-bumping granules and insoluble impurities. A fluted filter paper is used since it provides a much larger surface area than the usual filter paper cone and makes for a faster filtration. Prior to filtering the hot solution, the fluted filter paper, glass funnel and conical flask should be warmed to reduce the risk of crystals separating out on the filter paper and in the stem of the funnel. This can be done by heating the filtration equipment in an oven or by adding a little solvent to the conical flask and placing the equipment on a hot plate – as the solvent boils and refluxes, the flask, funnel and filter paper are heated. The hot solution is quickly poured through the pre-heated filtration apparatus and provided the operation has been carried out successfully, no crystals should appear at this stage. If they do appear on the filter paper or in the funnel stem, then they must be scraped back into the first flask, re-dissolved and re-filtered. Should any crystals be present in the filtered solution, the flask should be placed back on the hot plate and reheated to dissolve them.

A fluted filter paper

Once a clear filtered solution has been obtained it is set aside and left undisturbed until it slowly cools to room temperature. While it is cooling, the flask should be covered with a watch glass or filter paper to keep out dust particles. Slow cooling of the saturated solution is necessary to promote the formation of **pure** crystals. This is because crystallisation is a selective process and only molecules of the correct shape fit into the growing crystal lattice. Molecules of impurities will have a different shape and won't fit the lattice and as a result they remain dissolved in the mother-liquor. If the saturated solution cooled too quickly then the molecules of impurities become surrounded and trapped within the crystals. Not only does the rate of cooling control the purity of the crystals, it also dictates their size: the slower the rate of cooling the larger and purer will be the crystals.

When the solution has cooled completely, and this could take up to an hour, a good crop of crystals should have appeared in the flask. If none appears then it may be that the solution is not saturated, ie too much solvent has been used in the recrystallisation process. In such a case, some of the solvent can be boiled off in order to concentrate the solution and this can be re-cooled. If crystallisation still doesn't occur, there are a number of tactics available to induce the process. One way is to cool the saturated solution by placing the flask in an ice/water bath or in a fridge. Alternatively, a minute amount of the crude material or pure compound (if it is available) can be added to the saturated solution. The tiny particles of solid serve as nuclei around which the crystals can grow. This method is known as **seeding** and the solid particles that are added are referred to as **seed crystals**. Yet another way

of inducing crystal formation is to scratch the inside wall of the flask at the liquid surface using a glass rod. The tiny particles of glass that are dislodged act as nuclei for crystal growth.

When crystallisation is complete, the mixture of crystals and mother-liquor is filtered at the water pump, using a Buchner funnel and flask or Hirsch funnel and filter tube (see page 29). The crystals are then washed with a small portion of ice-cold solvent to remove traces of mother-liquor from their surfaces. With the water pump still running, air is drawn through the crystals to dry them partially. After transferring the crystals to a pre-weighed clock glass, drying can be continued in an oven at a temperature of at least 20°C below the expected melting point. However, under these conditions many organic solids have a tendency to sublime and so it is probably safer to dry the crystals at room temperature but in a desiccator containing anhydrous calcium chloride or silica gel. Once dry, the crystals and clock glass are re-weighed. This is necessary so that the percentage yield of product can be calculated.

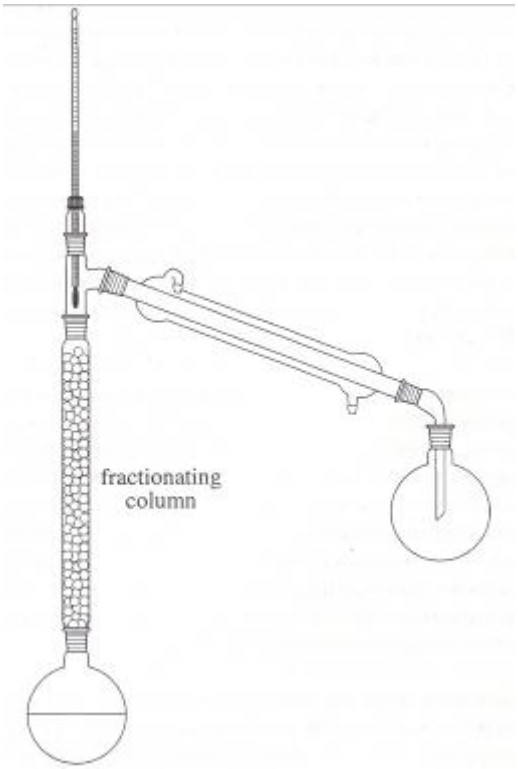
A second crop of crystals can often be extracted from the mother-liquor. This is achieved by transferring the mother-liquor from the Buchner flask or filter tube to a conical flask and heating it on a hot plate to drive off about half the solvent. On cooling the saturated solution, crystallisation takes place and the crystals are isolated by filtration and washed and dried in the usual way. Although the second crop of crystals may not be quite as pure as the first, the advantage of taking a second crop is that the percentage yield will be boosted.

In a **liquid** product, the most common impurity present is generally water and it can be removed using a **drying agent** such as anhydrous calcium chloride or anhydrous magnesium sulfate. In practice, a small amount of the powdered or granular drying agent is added directly to the crude liquid sample contained in a conical flask. The mixture is initially swirled and then left to stand for 10–15 minutes. If at this point the liquid is completely clear with no hint of cloudiness then we can assume that the product has been successfully dried. The liquid is separated from the drying agent by decanting it or filtering it into a round-bottomed flask. The sample is now ready for further purification by **distillation**. The type of distillation to be performed will depend largely on the nature of the remaining impurities and in particular their **volatility**. If they are much less volatile than the desired product then a **simple distillation** will suffice.

A few anti-bumping granules are added to the liquid sample in the round-bottomed flask and the apparatus illustrated on page 30 is assembled, making sure that the bulb of the thermometer is correctly positioned. Cold water is allowed to circulate through the condenser and the heating mantle is switched

on. The rate of heating should be adjusted so that the liquid boils gently and the distillation rate is slow – about one or two drops per second. The liquid, which distils within a narrow temperature range (about 5°C) that embraces the boiling temperature of the pure product, is collected in a pre-weighed receiving flask. The flask and purified product are then reweighed.
To minimise loss of product through evaporation the usual precaution of placing the receiving flask in an ice/water bath should be taken.

If the impurities in the crude liquid sample are volatile then **fractional distillation** rather than simple distillation must be carried out. The procedure is identical to that described above but the apparatus differs slightly in that a **fractionating column** is inserted vertically between the distillation flask and the still head.



There are various types of fractionating column but the one illustrated above is packed with lots of tiny glass beads. Fractional distillation is a much more effective way of ridding a liquid product of impurities than simple distillation. The liquid mixture goes through a multi-step distillation as it rises up the fractionating column and a much 'cleaner' separation of the components takes place.

Identification

Once the desired product of an organic reaction has been separated and purified, the next step is to confirm that it is the compound we had set out to prepare. There are numerous ways of doing this but we shall concentrate on just a few.

If the product is a **solid**, we can determine its **melting point** and compare it with the accepted or literature value. If these are in close agreement, we can be fairly sure, although not certain, of the identity of the compound. The reason for the doubt is that lots of other compounds will share the same melting point. However, the chance of any one of these being formed in the reaction instead of our desired product is extremely remote.

The melting point of a solid is defined as the temperature at which it changes into a liquid. In practice, what we measure is the temperature at which it just starts to melt and the temperature at which it has just completely liquefied. In other words, we measure a melting point range rather than a single melting temperature and when we report the melting point, it is the temperature range that must be quoted, eg 148–150°C. If a substance is pure then it will melt entirely within a range of about 1°C, ie it will have a definite and sharp melting point. However, if the substance is impure then the melting point will be indefinite and occur over several degrees. The presence of impurities in a substance lowers its melting point and broadens its melting point range, and the greater the amount of impurity present the greater will be the depression of the melting point. Hence, measuring a melting point not only helps to characterise a substance, but also provides confirmation of its purity.

The detailed experimental procedure involved in determining the melting point of a substance is outlined below.

A few dry crystals of the substance are placed on a watch glass and crushed to a fine powder using a glass rod or spatula. A glass capillary tube – to contain the powdered sample – is prepared by sealing off one end of the tube. This is done by touching one end of the tube to the base of a blue Bunsen flame – the glass melts and closes off that end. Once the tube has cooled, some of the sample is introduced. This is achieved by pushing the open end of the tube into the sample, trapping some of the powdered solid. The tube is then inverted and while holding it near the base, the sealed end is sharply tapped against the bench. The solid should fall to the bottom of the tube but if it doesn't, gently rub the sides of the tube with a small file. The filling procedure is repeated until there is 1–2 mm (no more) of solid in the tube.

With the capillary tube filled correctly, we can now measure the melting point of the solid. Several types of melting-point devices are available but

most contain a metal block in which the capillary tube and a thermometer can be accommodated. The metal block is normally heated electrically and the rate of heating controlled by means of a variable resistor. In addition, the apparatus is likely to have a light to illuminate the sample chamber within the block and an eyepiece containing a small magnifying lens to facilitate observation of the sample. With the filled capillary tube and thermometer in place, the temperature of the metal block is raised quite quickly to within 25°C of the expected melting point. Thereafter, the temperature is increased very slowly at a rate of about 2°C per minute. The thermometer reading is taken when the solid just begins to melt and then again when all the solid has just melted and only a clear liquid is observed.

To obtain an accurate melting point it is vitally important that over the last 25°C or so the temperature of the metal block is raised very, very slowly. If it is not, the melting point of the solid will be underestimated, ie the measured value will be lower than the true value. This is because the mercury in the thermometer takes time to respond to the rising temperature of the block. Consequently, the thermometer reading lags behind the temperature of the block and the more rapid the heating rate, the wider will be the gap between the two.

It was mentioned earlier that knowledge of the melting point of a compound doesn't allow us to identify it with absolute certainty. One way of removing any shadow of doubt is to carry out what is known as the **mixed melting point** technique. This involves mixing a pure sample of the compound we have prepared and a pure sample of the compound we think we have prepared. Roughly equal amounts of the two compounds are thoroughly ground together and the melting point of the intimate mixture is then measured in the usual way. If the melting point turns out to be sharp and close to the expected value, then the two compounds must be identical. In other words, the identity of the compound we have prepared has been confirmed. Had the two compounds not been the same then the melting point of the mixture would have been much lower and the melting range much broader. This results from the fact that each compound would act as an impurity of the other.

If our reaction product is a **liquid** rather than a solid then we can measure its **boiling point** to help us identify it. If this is close to the accepted value then our product is likely to be the compound we had set out to prepare.

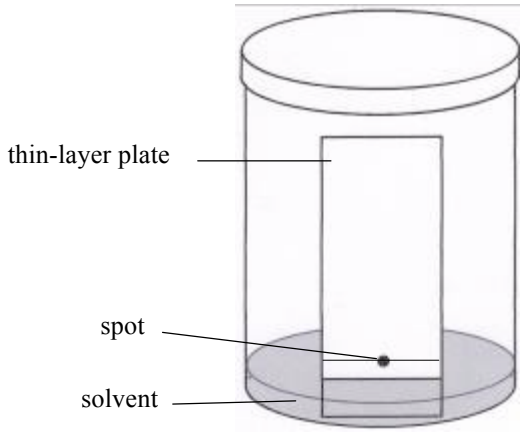
One way of determining the boiling point of a liquid is by a simple distillation using the apparatus illustrated on page 30. The round-bottomed flask is half-filled with the liquid and a few anti-bumping granules are added to ensure smooth boiling. The apparatus is assembled with the thermometer correctly positioned. The water to the condenser is turned on, and the flask

and its contents are heated using a heating mantle. Initially, the rate of heating can be quite rapid but once the liquid starts to boil, it should be reduced and adjusted so that the distillate collects in the receiving flask at a rate of a drop per second. Provided the liquid is pure and distilling steadily, the thermometer reading should remain constant. This constant temperature is the boiling point of the liquid.

There is one slight drawback in using boiling point to characterise our liquid product and it arises from the fact that boiling point varies with atmospheric pressure. The deviation between the observed boiling point and its true value can be quite significant – up to several degrees. Consequently, the number of compounds having a boiling point in the vicinity of the observed value could be very large. However, they are unlikely to be produced in the reaction and so most, if not all, of them can be eliminated. It would have been quite a different matter had the liquid been an unknown.

One way of removing the uncertainty attached to the identity of a liquid product is to convert it into a **solid derivative** and determine the melting point of the derivative. This can then be compared with the melting points of known derivatives. Melting points are much more reproducible than boiling points since their variation with atmospheric pressure is negligibly small.

Another powerful tool that is commonly used in identifying a compound is **thin-layer chromatography** (TLC). TLC, like all chromatography techniques, depends on the distribution of substances between two phases: a mobile phase and a stationary phase. TLC uses glass or plastic plates coated with a thin layer of finely ground silica gel or aluminium oxide as the stationary phase. A pencil line is lightly drawn about 1 cm from the bottom of the plate and a small amount of the substance being analysed is dissolved in about 2 cm^3 of a volatile solvent such as propanone or dichloromethane. Using a capillary tube, some of this solution is spotted onto the centre of the pencil line and left to dry. This should be repeated two or three more times. It is important that the final spot should be about 1–2 mm in diameter. Once the spot is dry the plate is placed in a closed chamber with the lower edge (near the applied spot) immersed in a shallow layer of solvent, ie the mobile phase. It is important that the solvent level is below the line with the spot on it and that the chamber is closed completely. The latter ensures that the chamber is

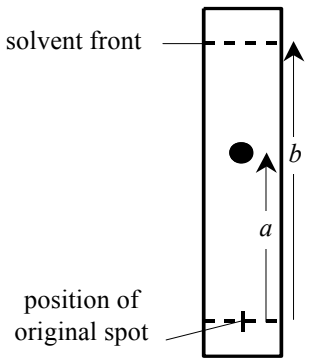


saturated with solvent vapours. The solvent rises through the stationary phase by capillary action and carries with it the substance being analysed. How far that substance moves depends on how well it binds to the stationary phase and how well it dissolves in the solvent. The more tightly a substance is held to the stationary phase and the less soluble it is in the solvent, the more slowly it moves up the plate. The thin-layer plate is removed from the chamber when the solvent front is about 1 cm from the top of the plate. The position of the solvent front is marked immediately with a pencil before the solvent evaporates. The plate should then be left to dry in a fume cupboard. If the substance is colourless then its final position on the plate will not be seen but there are a few ways in which this problem can be overcome. One way is to use a plate impregnated with a fluorescent indicator and then expose it to UV light. The plate will glow apart from the spot where the substance is and this can be marked by drawing a pencil circle around it. In another method the dried plate is placed in a closed container containing a few crystals of iodine. The iodine vapour in the container may either react with the substance spot on the plate or adhere to it more strongly than the rest of the plate. Either way, the substance you are interested in will show up as a brownish spot.

Under a definite set of experimental conditions for a thin-layer chromatographic analysis, a given substance will always travel a fixed distance relative to the distance travelled by the solvent front. This ratio of distances is called the ***R*_f value**. The term R_f stands for '**r**atio to **f**ront' and is expressed as a decimal fraction:

$$R_f = \frac{\text{distance travelled by substance}}{\text{distance travelled by solvent front}}$$

Let's illustrate how we would calculate the R_f value of a substance given its chromatogram:



$$R_f = \frac{a}{b}$$

The R_f value for a substance depends on its structure and is a physical characteristic of the compound, just as a melting point is a physical characteristic. However, identifying a substance purely from its R_f value is unreliable. In practice, it is more usual to carry out a thin-layer chromatographic analysis with the product you prepared along with a pure sample of the compound you think you prepared. If the resulting chromatogram shows two spots at the same distance from the origin, ie with the same R_f value, then the two compounds are identical.

Percentage yield

An organic preparation is incomplete unless the **percentage yield** of pure product has been calculated and reported. Percentage yield is defined as:

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

The actual yield (often shortened to yield) is the mass of pure product obtained in the reaction while the theoretical yield is the maximum mass that might have been expected. The latter can be calculated from knowledge of the stoichiometric equation for the reaction and the mass of the limiting reactant, ie the one that is not in excess.

The percentage yield always falls short of 100% but there are many good reasons for this:

- The reaction may be **reversible**, in which case a state of equilibrium will be reached. While we'll never get 100% conversion of reactants into products in a reversible reaction, some tactics can be adopted to maximise the yield. For example, we could ensure that the other reactants are used in large excess compared to the limiting one or it may be possible to add a reagent that reacts with one of the products. Both measures would encourage the equilibrium position to move to the right and so improve the yield of product.

- **Side reactions** of many kinds may occur. In other words, the limiting reactant undergoes other reactions in addition to the desired one. Formation of a side product inevitably reduces the yield of the main product.

- **Mechanical loss** of the product is likely to occur. For example, during isolation and purification the product may be transferred from one container to another on numerous occasions. As a result, some of it will fail to reach the final container. Product loss will also occur in

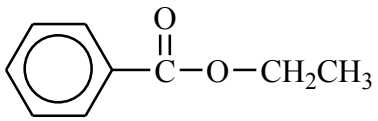
recrystallisation since some will remain in the mother-liquor. Loss can also occur through evaporation and this would be the case if the product was a volatile liquid. While mechanical loss of product cannot be eliminated, good experimental technique will minimise it.

Experiments

Experiment 1: Preparation of benzoic acid by hydrolysis of ethyl benzoate

Introduction

Benzoic acid can be prepared by the alkaline hydrolysis of the ester, ethyl benzoate:



If sodium hydroxide is used, then the residual solution will contain sodium benzoate. Insoluble benzoic acid can be displaced from this solution by acidification. It can then be filtered off and purified by recrystallisation. The percentage yield of benzoic acid can be calculated. The purity and identity of the final sample can be checked by measuring its melting point and mixed melting point, and by thin-layer chromatography.

Requirements

100 cm^3 round-bottomed flask
cork ring
condenser
heating mantle
100 cm^3 measuring cylinder
250 cm^3 beaker
glass filter funnel
thermometer
balance (accurate to 0.01 g)
hot plate
Buchner funnel and flask
water pump
filter papers
clock glass
glass stirring rod
dropper
oven
capillary tubes
melting point apparatus
chromatography chamber
TLC plate

ethyl benzoate
2 mol l^{-1} sodium hydroxide
5 mol l^{-1} hydrochloric acid
blue litmus paper or pH paper
anti-bumping granules
deionised water
sample of pure benzoic acid
iodine
dichloromethane
ethyl ethanoate

test-tubes
UV lamp

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
Ethyl benzoate is of low volatility and flammability. It irritates the eyes and is harmful if ingested in quantity.
2 mol l^{-1} sodium hydroxide is corrosive to the eyes and skin. Gloves and goggles should be worn.
5 mol l^{-1} hydrochloric acid is irritating to the eyes, lungs and skin. Wear gloves.
Benzoic acid is of low volatility and flammability. It may be harmful if ingested in quantity.
Dichloromethane irritates the eyes and skin, and is at its most harmful if inhaled. Wear gloves.
Ethyl ethanoate is irritating to the eyes, is volatile and can irritate the respiratory system. It is highly flammable. Wear gloves.

Procedure

1. Weigh a 100 cm^3 round-bottomed flask supported on a cork ring. To the flask add about 5 g of ethyl benzoate and reweigh the flask and its contents.
2. To the ethyl benzoate add approximately 50 cm^3 of 2 mol l^{-1} sodium hydroxide and a few anti-bumping granules.
3. Set up the apparatus for heating under reflux. Using a heating mantle, reflux the reaction mixture until all the oily drops of the ester have disappeared. This may take 45–60 minutes.
4. Allow the apparatus to cool and then transfer the reaction mixture to a 250 cm^3 glass beaker.
5. Slowly and with stirring add 5 mol l^{-1} hydrochloric acid to the reaction mixture to precipitate out the benzoic acid. Continue adding the acid until no more precipitation takes place and the mixture turns acidic (test with blue litmus paper or pH paper). About 30 cm^3 of acid will be required.
6. Allow the mixture to cool to room temperature and filter off the precipitate at the water pump. Wash the crude benzoic acid with a small volume of water.
7. Transfer the crude benzoic acid to a 250 cm^3 beaker and recrystallise it from about 100 cm^3 of water.
8. Filter off the crystals of benzoic acid at the water pump and wash them with a small volume of water. Allow air to be drawn through the crystals for a few minutes in order to partially dry them.

9. Weigh a clock glass and transfer the crystals to it. Dry the crystals in an oven at about 70°C and then reweigh the clock glass and crystals.
10. Calculate the percentage yield of benzoic acid.
11. Determine the melting point of the benzoic acid product.
12. Grind a 50:50 mixture of your product and a pure sample of benzoic acid, and determine the mixed melting point. This will give you some indication of the purity of the benzoic acid you prepared.
13. Take a TLC plate and using a pencil lightly draw a line across the plate about 1 cm from the bottom. Mark two well-spaced points on the line.
14. Place small amounts (about a third of a spatulaful) of your benzoic acid product and a pure sample of benzoic acid in two separate test-tubes.
15. Add about 1 cm^3 of ethyl ethanoate to each of the test-tubes to dissolve the benzoic acid samples.
16. Use capillary tubes to spot each of the two samples onto the TLC plate. Allow to dry and repeat two or three more times.
17. After the spots have dried, place the TLC plate into the chromatography chamber, making sure that the pencil line is above the level of the solvent (dichloromethane). Close the chamber and wait until the solvent front has risen to within a few millimetres of the top of the plate.
18. Remove the plate from the chamber, immediately marking the position of the solvent front, and allow it to dry.
19. Place the TLC plate in a beaker containing a few iodine crystals and cover the beaker with a clock glass. Once any brownish spots appear, remove the plate and lightly mark with a pencil the observed spots. Alternatively, observe the dried TLC plate under UV light and lightly mark with a pencil any spots observed.
20. Calculate the R_f values of the spots. This will give you some indication of the purity of the benzoic acid you have prepared.

Experiment 2: Preparation of cyclohexene from cyclohexanol

Introduction

Cyclohexene can be prepared by dehydrating cyclohexanol using concentrated phosporic acid. The product can be separated from the reaction mixture by distillation, and after purification it can be weighed and the percentage yield determined.

Requirements

50 cm^3 round-bottomed flasks
cork ring
condenser
still head
receiver adapter
thermometer adapter
thermometer
balance (accurate to 0.01 g)
heating mantle
250 cm^3 separating funnel
10 cm^3 measuring cylinder
50 cm^3 conical flask
dropper
test-tube and rack

cyclohexanol
85% phosphoric acid
saturated sodium chloride solution
anhydrous calcium chloride
anti-bumping granules
bromine solution

Hazcon

Wear eye protection and if any chemical splashes on the skin, wash it off immediately.
Cyclohexanol (including its vapour) is harmful to the eyes, lungs and skin, and is harmful if swallowed. It is flammable and is a suspected carcinogen. Wear gloves.
85% phosphoric acid is corrosive; it burns and irritates the eyes and skin. It is a systemic irritant if inhaled and if swallowed causes serious internal injury. Wear gloves.
Anhydrous calcium chloride irritates the eyes, lungs and skin. Wear gloves.
The product, cyclohexene, is highly flammable and its vapour is moderately toxic to the eyes, skin and respiratory system. Wear gloves. At the end of the experiment, dispose of the cyclohexene since it may form unstable peroxides if stored.
Bromine solution causes burns and is toxic. Wear gloves.

Procedure

1. Weigh a 50 cm^3 round-bottomed flask supported on a cork ring. To the flask add approximately 20 g of cyclohexanol and reweigh the flask and its contents.
2. To the cyclohexanol add dropwise with swirling about 8 cm^3 of 85% phosphoric acid.
3. Add a few anti-bumping granules to the reaction mixture and set up the apparatus for distillation. Gently heat the mixture for about 15 minutes making sure it doesn't boil. Raise the temperature and distil the mixture very slowly, collecting the liquid which comes over between 70 and 90°C.
4. Pour the distillate into a separating funnel and add about an equal volume of saturated sodium chloride solution. Stopper the funnel and shake the contents vigorously.
5. Clamp the separating funnel and allow the two layers to separate.
6. Remove the stopper from the funnel and run off the lower aqueous layer into a beaker and dispose of it down the sink.
7. Run the top layer (the crude alkene) into a small conical flask and add a few pieces of anhydrous calcium chloride. Stopper the flask and shake the mixture for a few minutes until the liquid is clear.
8. Weigh a dry 50 cm^3 round-bottomed flask in which to collect the pure cyclohexene.
9. Decant the alkene into another dry 50 cm^3 round-bottomed flask and add a few anti-bumping granules. Distil the alkene very slowly, collecting the liquid which comes over between 81 and 85°C in the pre-weighed flask. To cut down loss of the volatile cyclohexene during distillation, the receiving flask could be placed in an ice bath.
10. Weigh the flask and product.
11. Carry out a test to show that the product is unsaturated.
12. Calculate the percentage yield.