Week 11 Organic Reactions

1. Reactions of alkanes

- An alkane molecule has a carbon-carbon ‘backbone’ which is surrounded by carbon–hydrogen bonds.
- Since all the carbon atoms have the same electronegativity, and hydrogen and carbon have similar electronegativity, the alkane molecule is non-polar.
- The alkanes are insoluble in water but are soluble in non-polar solvents.
- The weak dispersion forces between molecules results in their low melting and boiling points.
- The stability of the carbon–carbon bonds and the non-polar nature of the molecules means that alkanes are very resistant to reaction.
- Most reactions involving alkanes are either **combustion** or **substitution**.

Combustion

- Combustion reactions involving alkanes release large amounts of heat energy hence their use as fuels.
- Methane is the major component in natural gas,
  $CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g)$ + energy

  And octane is an important component of petrol.
  $2C_8H_{18}\,(g) + 25O_2(g) \longrightarrow 16CO_2\,(g) + 18H_2O\,(g)$ + energy

Substitution reactions

When one or more of the hydrogen atoms in an alkane is replaced by a different atom or **functional group**.
This involves breaking the carbon-hydrogen bonds and making new bonds with the substituting atom or group.

Example
Chloroethane (CH_3CH_2Cl) is a gas at room temperature and is used as a local anaesthetic spray.

- It can be produced by heating mixtures of chlorine and ethane; or, the reaction can be initiated by exposing the gas mixture to ultraviolet light.
- In both methods, the chlorine molecule, Cl_2, breaks into separate chlorine atoms.
- The unstable (with only seven outer-shell electrons) chlorine free radicals attack the carbon-hydrogen bonds in the ethane.
- This results in a mixture of chlorinated alkanes, including CH_3CH_2Cl, CH_3CHCl_2, CH_3CCl_3 and CH_2ClCH_2Cl. The amounts of each product depend on the relative starting amounts of chlorine and ethane.

Simplified reaction for the manufacture of chloroethane:

$$CH_3CH_3(g) + Cl_2(g) \xrightarrow{\text{heat or light}} CH_3CH_2Cl(g) + HCl(g)$$

The chlorination of alkanes can be represented by the general equation:

$RH + Cl_2 \rightarrow RCl + HCl$
where R represents an alkyl group

A reaction like this, in which one atom is replaced by another atom or group of atoms, is called a **substitution reaction**. In this instance, a chlorine atom has replaced a hydrogen atom in ethane.

summary 10.1

- Alkanes undergo combustion and substitution reactions.
- Carbon atoms are oxidised in combustion reactions and heat energy is produced.
- In substitution reactions, one or more hydrogen atoms is replaced by other atoms or groups of atoms.

2. Reactions of alkenes

Ethene (known in industry as ethylene), is the first member of the homologous series of alkenes.
Ethene C_2H_4:
- is unsaturated
- is a non-polar molecule
- is insoluble in water
- is a flammable gas
- participates in addition reactions
- polymerises to produce polyethene.

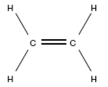


Figure 10.2
The structure of the ethene molecule.

Since ethene is a small, non-polar molecule, the only attractive forces between its molecules are dispersion forces and ethene therefore has a very low boiling temperature: –104°C.

With its double covalent bond, Ethene reacts more readily, and with more chemicals, than ethane (CH_3CH_3), which contains only single bonds.

Addition reactions of alkenes

Ethene is an extremely useful substance because of its ability to undergo addition reactions.
The reactions of ethene usually involve *addition* of a small molecule to produce a single product.

For example, it reacts with bromine solution (Br_2 dissolved in an organic solvent).
This reaction, in which the red-brown colour of bromine disappears as it reacts with the alkene, is used as a general test for unsaturation.
This type of reaction is known as an **addition reaction**.
During addition reactions the double carbon–carbon bond is converted to a single bond.

Figure 10.4
Addition of bromine to ethene.

Ethanol can be produced by an addition reaction of ethene and water using a catalyst.

Commercial manufacture of ethanol is via the addition reaction of steam and ethene using a solid phosphoric acid catalyst.
It is a one-step process that uses little energy, apart from initial heating.

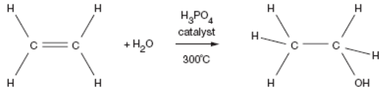


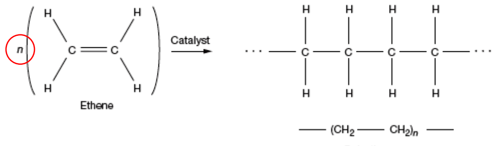
Figure 10.5
The formation of ethanol from ethene.

The reaction of ethene with steam is often described as a **hydrolysis** reaction. Hydrolysis reactions involve water as a reactant.

The other alkenes undergo similar addition reactions to produce **alkanols** and **chloroalkanes**.

Addition polymerization

A type of addition reaction of ethene is involved in making polyethene.



$—(CH_2—CH_2)_n—$

Figure 10.6
The formation of polyethene by addition polymerisation.

The number *n* in this reaction is very large - several thousand or more.
This type of reaction is known as **addition polymerisation**.
When the polymer is being formed the ethene molecules add to the end of growing polymer chains.

Polyvinyl chloride (PVC) has many uses and often replaces materials such as glass, ceramics, rubber and steel.
Additives that modify the properties of PVC have enabled it to become one of our most versatile polymeric materials, and it is used in an enormous range of articles.
You will be familiar with a number of these, such as insulation around electrical cables and many kinds of packaging.

Polyvinyl chloride is manufactured by an addition polymerisation reaction from the monomer vinyl chloride (chloroethene)

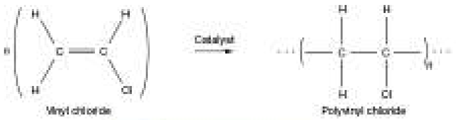


Figure 10.7
Production of polyvinyl chloride from vinyl chloride.

Polystyrene is another polymer for which there is a wide range of applications, including packaging.
It is made from the monomer styrene which in turn is made from ethene.
Styrene is also mixed with acrylonitrile and butadiene to make ABS plastic, which is used to make hard hats and bicycle helmets.
ABS is an example of a **copolymer** -a polymer made from more than one monomer.

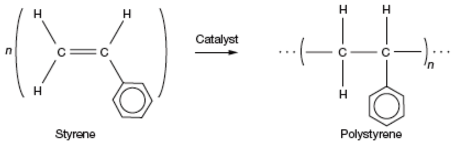


Figure 10.8
Polymerisation of styrene to form polystyrene.

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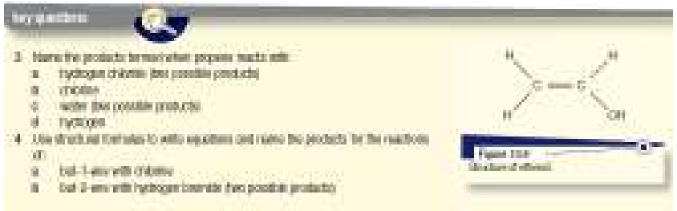
summary 10.2

- Alkenes participate in addition reactions.
- The carbon–carbon double bond is converted to a single bond during addition reactions.
- Alkenes react with chlorine to form chloroalkanes.
- Alkenes react with water to form alkanols.
- Alkenes undergo addition polymerisation reactions.



Key questions

3 Name the products formed when propene reacts with:
  a hydrogen chloride (two possible products)
  b chlorine
  c water (two possible products)
  d hydrogen

4 Use structural formulas to write equations and name the products for the reactions of:
  a but-1-ene with chlorine
  b but-2-ene with hydrogen bromide (two possible products)

Figure 10.9
Structure of ethenol

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3. Reactions of functional groups

Reactions of chloroalkanes

A chloroalkane is polar.

Electrons in the carbon-chlorine bond are attracted towards the more electronegative chlorine atom.
This makes the carbon atom at the other end of the bond susceptible to attack by negatively charged ions (anions).

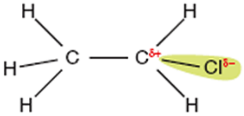

Figure 10.10
Structural formula of chloroethane. Hydrogen has electronegativity of 2.1, carbon is 2.5 and chlorine is 3.2.

For example chloromethane is converted to methanol when it is reacted with hydroxide ions. The chlorine atom is *substituted* by an OH functional group to form methanol.

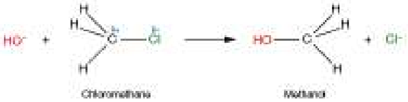

Figure 10.11
Reaction of chloromethane with hydroxide ions.

Ethanol is formed when chloroethane reacts with water.

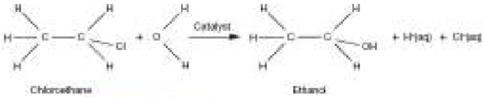

Figure 10.12
Reaction of chloroethane with water

Chloroalkanes will also react with ammonia to form amines:

$RCl + NH_3 \longrightarrow RNH_2 + HCl$

The chloroalkanes higher in the homologous series undergo similar substitution reactions.

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4. Reactions of alkanols

Ethanol is the most widely used alkanol.

Alkanols can undergo substitution reactions.

The amino functional group can be introduced into the alkane chain by a substitution reaction between ammonia and an alkanol.

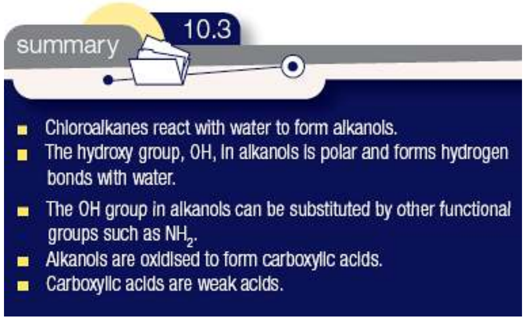
For example, ethylamine is formed by passing ammonia and ethanol vapour over alumina (aluminium oxide) heated to about 400°C:

$CH_3CH_2OH\ (g) + NH_3\ (g) \longrightarrow CH_3CH_2NH_2\ (g) + H_2O\ (g)$

Alkanols can be oxidised to form **carboxylic acids**:

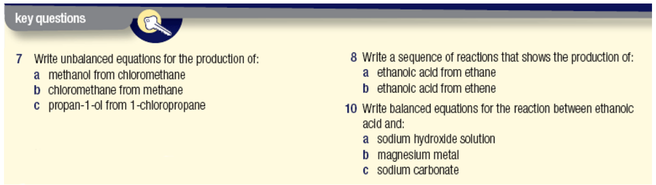
$$CH_3CH_2OH(aq) \xrightarrow{O_2\,(g)} CH_3COOH(aq)$$

- Not all alkanols will oxidise to form carboxylic acids.
- The position of the OH function group in an alkanol determines the oxidation product.
- Carboxylic acids are synthesised from the oxidation of primary alkanols.
- In primary alkanols the OH functional group is attached at the end of a chain of carbon atoms or at the end of a side chain, *i.e.* primary alkanols have a –CH_2OH grouping.



summary 10.3

- Chloroalkanes react with water to form alkanols.
- The hydroxy group, OH, in alkanols is polar and forms hydrogen bonds with water.
- The OH group in alkanols can be substituted by other functional groups such as NH_2.
- Alkanols are oxidised to form carboxylic acids.
- Carboxylic acids are weak acids.



key questions

7 Write unbalanced equations for the production of:
  a methanol from chloromethane
  b chloromethane from methane
  c propan-1-ol from 1-chloropropane

8 Write a sequence of reactions that shows the production of:
  a ethanoic acid from ethane
  b ethanoic acid from ethene

10 Write balanced equations for the reaction between ethanoic acid and:
  a sodium hydroxide solution
  b magnesium metal
  c sodium carbonate

Esters: Sweet flavors and strong aromas

Esters are a group of organic compounds responsible for some of the natural and synthetic flavors and smells in ice-creams, lollies, flowers, fruits, and perfumes.

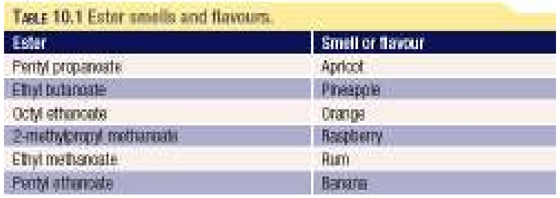


TABLE 10.1 Ester smells and flavours.

Ester	Smell or flavour
Pentyl propanoate	Apricot
Ethyl butanoate	Pineapple
Octyl ethanoate	Orange
2-methylpropyl methanoate	Raspberry
Ethyl methanoate	Rum
Pentyl ethanoate	Banana

Low molecular weight esters:
They have low boiling points that allow them to evaporate easily and reach your nose - volatile and smelly.

High molecular weight esters:
Are oils and waxes.

Condensation reactions are those that involve the combination of two reactants and the elimination of a small molecule, such as water

- Esters are made by such as reaction between a carboxylic acid and an alkanol.
- For example, gently heating a mixture of ethanol and pure ethanoic acid with a trace amount of sulfuric acid (added as a catalyst) produces an ethyl ethanoate and water.

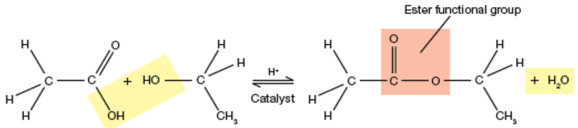


Figure 10.19
Production of the ester ethyl ethanoate from ethanol and ethanoic acid.

Ethyl ethanoate is used as artificial flavouring, a solvent in some paints, adhesives and nail varnish.

Generally:

Figure 10.20
A general equation for ester formation. The OH group in the acid is replaced with the –OR′ of the alkanol.

Esters have two-part names:
The first part derived from the name of the alkanol from which it is made, where 'yl' replaces 'anol'.
The second part comes from the carboxylic acid, where 'ic acid' is replaced by the suffix 'ate'.
Thus, the ester formed from ethanol and ethanoic acid is eth*yl* ethano*ate*

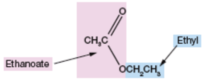


Figure 10.21
Naming esters.

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summary 10.4

- Carboxylic acids react with alkanols to form esters and water.
- The reaction between carboxylic acids and alkanols is called a condensation reaction.
- The name of an ester indicates the alkanol and acid from which it derived.
- The general formula of esters is RCOOR′.

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key questions

11 Draw the structural formulas of the following esters and name them.
  a CH_3COOCH_3
  b $CH_3COOCH_2CH_3$
  c $CH_3CH_2COOCH_2CH_3$

12 Write equations that describe the formation of an ester to smell like:
  a pineapple (ethyl butanoate)
  b rum (ethyl methanoate)

12 a $CH_3CH_2CH_2COOH(l) + CH_3CH_2OH(l) \xrightarrow{H_2SO_4} CH_3CH_2CH_2COOCH_2CH_3(l) + H_2O(l)$

b $HCOOH(l) + CH_3CH_2OH(l) \xrightarrow{H_2SO_4} HCOOCH_2CH_3(l) + H_2O(l)$

Reaction pathways

Organic chemists are highly skilled:

- properties needed for a particular purpose noted.
- appropriate molecular structures are devised.
- an efficient method for converting a readily available starting material (often an alkene or an alkane) into the product required is devised.

The reaction pathway selected needs to take into account:

- the yield and purity of the products
- and also minimisation of any unwanted side-products and waste materials.
- time and cost factors.

There is a lot of current interest in working out greener synthetic routes that minimise waste, use more environmentally friendly solvents, require less energy, and help to preserve the world's resources.

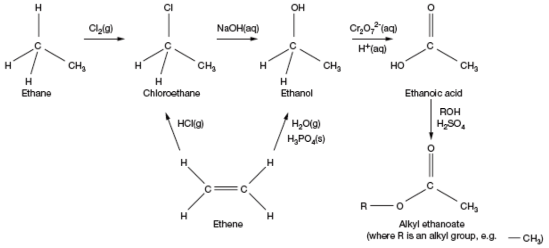


Figure 10.26
Reaction pathways based on ethane and ethene.

Example: Synthesis of ethyl propanoate

Starting materials required to be alkanes or alkenes.

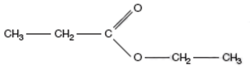


Figure 10.27
Structure of ethyl propanoate.

The structure of the compound indicates that it is an ester produced by the condensation reaction between **propanoic** acid and **ethanol**.

Therefore, propanoic acid and ethanol are required as feed chemicals for the production of ethyl propanoate.

Routes for ethanol production

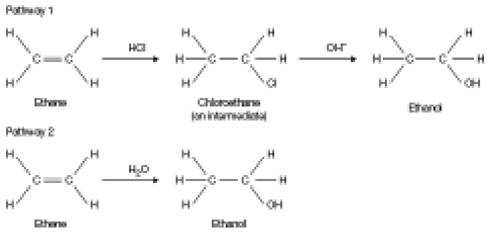


Figure 10.28
Synthetic pathways for ethanol.

Preparation of propanoic acid

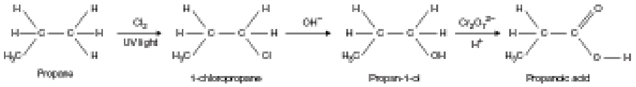


Figure 10.29
Synthesis of propanoic acid.

It is prepared by the oxidation of the primary alkanol propan-1-ol.

This in turn can be formed by the reaction of 1-chloropropane with sodium hydroxide.

1-chloropropane can be prepared by reacting propane with chlorine.

The substitution reaction of propane is preferable to an addition reaction of propene because the addition of HCl to propene will result in the formation of unwanted 2-chloropropane.

A condensation reaction is then used to prepare ethyl propanoate from ethanol and propanoic acid.

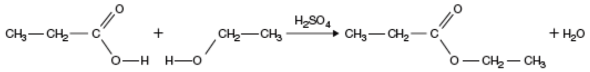


Figure 10.30
Synthesis of ethyl propanoate.

Considerations when devising a synthesis

- The structure of the required compound or target molecule is studied and the functional group(s) are identified.
- A synthetic pathway is devised using knowledge of the reactions of functional groups.
- The synthesis may require the preparation of a number of intermediate compounds.
- More than one possible pathway may need to be considered as a desired product may be synthesised via number of pathways.
- The formation of isomers and other by-products also needs to be considered.
- The methods of separation of the desired intermediate and final product from isomers and other by-products must be determined.

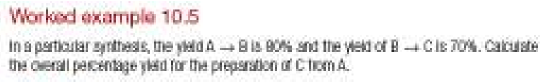
The yield must also be taken into account, as not all of the reactants are necessarily converted to product. For example, in the reaction:

$CH_3CH_2Cl + OH^- \longrightarrow CH_3CH_2OH + Cl^-$

6.45 g of chloroethane should produce 4.60 g of ethanol if all the chloroethane was converted to ethanol.

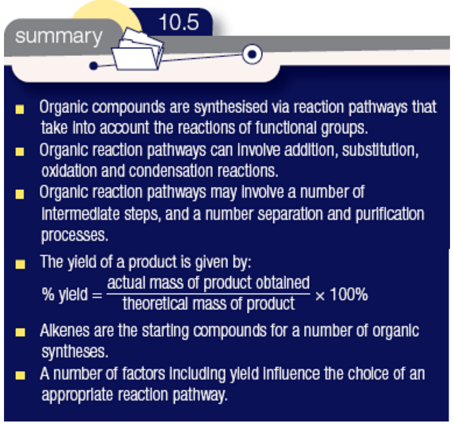
If only 2.30 g of ethanol was obtained then the yield would be 50%.

Where there are a number of intermediate steps involved in a synthesis, the yield for each step must be taken into account. A low yield in one of the intermediate reactions can have a dramatic effect on the overall yield.



Worked example 10.5

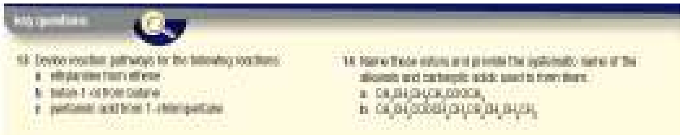
In a particular synthesis, the yield A → B is 80% and the yield of B → C is 70%. Calculate the overall percentage yield for the preparation of C from A.



- Organic compounds are synthesised via reaction pathways that take into account the reactions of functional groups.
- Organic reaction pathways can involve addition, substitution, oxidation and condensation reactions.
- Organic reaction pathways may involve a number of intermediate steps, and a number separation and purification processes.
- The yield of a product is given by:

$$\% \text{ yield} = \frac{\text{actual mass of product obtained}}{\text{theoretical mass of product}} \times 100\%$$

- Alkenes are the starting compounds for a number of organic syntheses.
- A number of factors including yield influence the choice of an appropriate reaction pathway.



Principles of fractional distillation

Fractional distillation is a technique used to separate liquids that have different boiling points.
It is commonly used in the laboratory to separate volatile liquids from a reaction mixture.

Industrial applications of fractional distillation include:

- separation of the fractions from crude oil.
- production of oxygen and nitrogen by the fractional distillation of liquid air.
- extraction of ethanol from water in the fermentation of sugar.

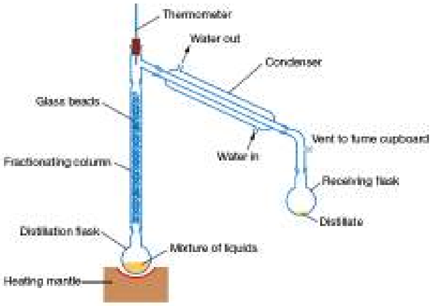


Figure 10.32
Fractional distillation apparatus used in the laboratory.

Fractional distillation is based on the principle that the concentration of the low boiling point component is higher in the vapour over a mixture of volatile liquids than it is in the liquid.

In fractional distillation the components of a mixture of volatile liquids are separated by what can be considered to be a succession of simple distillations.

1. When the mixture of liquids is heated in the distillation flask, mixed vapours rise up the fractionating column. These vapours contain a higher concentration of the more volatile component than the liquid in the distillation flask.
2. At some height in the fractionating column the temperature is low enough for condensation of the lowest boiling point to occur. As the condensed liquid trickles back down the column it is re-heated by vapours rising from the distillation flask, causing it to evaporate.
3. The resulting vapour has an even higher concentration of the low boiling point component.

4. This process of evaporation and condensation is repeated many times throughout the length of the column,
5. The concentration of the more volatile substance in the vapour increases in each evaporation–condensation cycle. At the same time the concentration of the less volatile (higher boiling point) substances in the distillation flask will increase.
6. When the vapour reaches the top of the fractionating column it will ideally consist of only the more volatile component. When the relatively pure component reaches the top of the fractionating column the temperature remains relatively stable. The material that condenses over a small temperature range near the boiling point of the substance of interest is collected.
7. It is not always possible to achieve a complete separation. Ethanol produced by the fermentation of sugar can be separated from water by fractional distillation but the distillate will always contain about 5% water.

Pure ethyl ethanoate can be extracted from a reaction mixture by fractional distillation.
The reaction mixture is heated in the distillation flask.
The vapour rises up the fractionating column.
The temperature at the top of the column slowly increases until it stabilises at about 57°C, which is the boiling point of ethyl ethanoate.
The fraction condensing over a small range of temperatures near the boiling point of ethyl ethanoate, 55°C - 59°C, is collected.

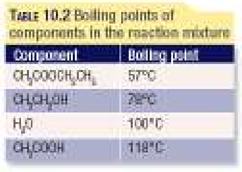
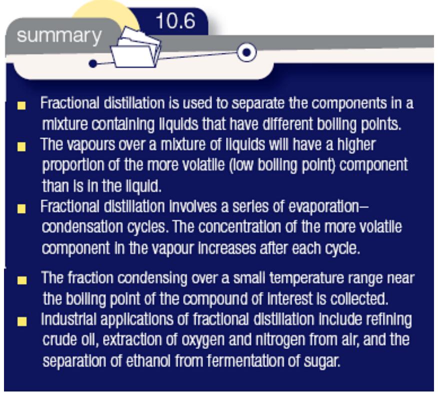


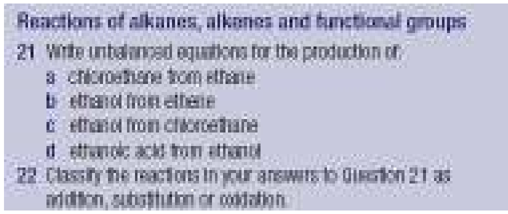
TABLE 10.2 Boiling points of components in the reaction mixture

Component	Boiling point
$CH_3COOCH_2CH_3$	57°C
CH_3CH_2OH	78°C
H_2O	100°C
CH_3COOH	118°C



summary 10.6

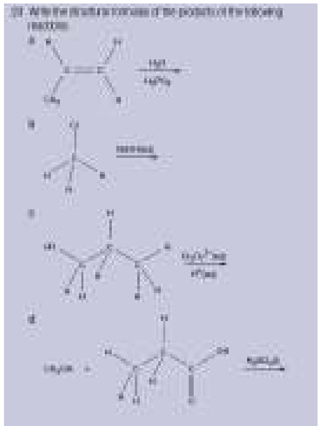
- Fractional distillation is used to separate the components in a mixture containing liquids that have different boiling points.
- The vapours over a mixture of liquids will have a higher proportion of the more volatile (low boiling point) component than is in the liquid.
- Fractional distillation involves a series of evaporation–condensation cycles. The concentration of the more volatile component in the vapour increases after each cycle.
- The fraction condensing over a small temperature range near the boiling point of the compound of interest is collected.
- Industrial applications of fractional distillation include refining crude oil, extraction of oxygen and nitrogen from air, and the separation of ethanol from fermentation of sugar.



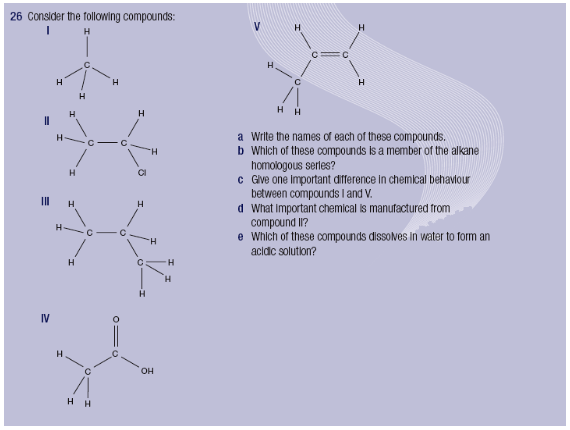
Reactions of alkanes, alkenes and functional groups

21 Write unbalanced equations for the production of:
  a chloroethane from ethane
  b ethanol from ethene
  c ethanol from chloroethane
  d ethanoic acid from ethanol

22 Classify the reactions in your answers to Question 21 as addition, substitution or oxidation.

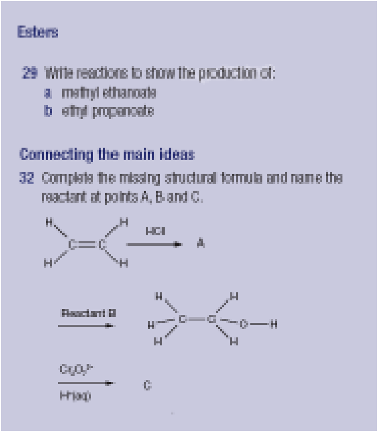


23 Write the structural formulas of the products of the following reactions:



26 Consider the following compounds:

a Write the names of each of these compounds.
b Which of these compounds is a member of the alkane homologous series?
c Give one important difference in chemical behaviour between compounds I and V.
d What important chemical is manufactured from compound II?
e Which of these compounds dissolves in water to form an acidic solution?



Esters

29 Write reactions to show the production of:
  a methyl ethanoate
  b ethyl propanoate

Connecting the main ideas

32 Complete the missing structural formula and name the reactant at points A, B and C.