

18: Organic Chemistry III

18A. Arenes

There are two major classes of organic chemicals
aliphatic : straight or branched chain organic substances
aromatic or arene: includes one or more ring of six carbon atoms with delocalised bonding.

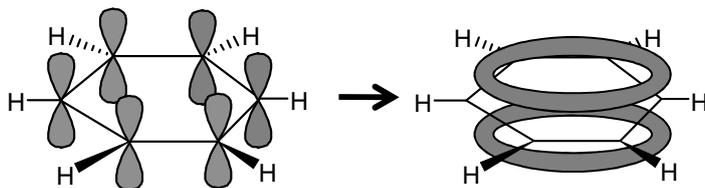
All of the organic substances we have looked at so far have been aliphatic

Benzene belongs to the aromatic class.

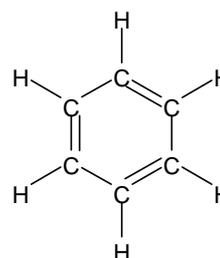
Benzene's Structure

The simplest arene is benzene. It has the molecular formula C_6H_6 . Its basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom.

Each C atom is bonded to two other C atoms and one H atom by single covalent bonds. This leaves one unused electron on each C atom in a p orbital, perpendicular to the plane of the ring. The six p electrons are delocalised in a ring structure above and below the plane of carbon atoms.



In 1865 Kekule suggested the following structure for Benzene consisting of alternate single and double covalent bonds between the carbon atoms.

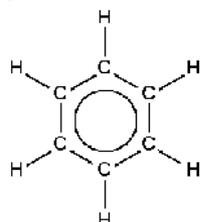


This structure is not correct. Evidence suggests that all the C-C bonds are the same length.

In formulae we draw a circle to show this delocalised system



Abbreviated formula



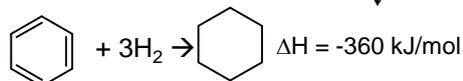
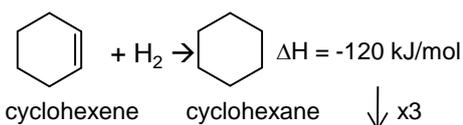
Displayed formula

The six electrons in the pi bonds are delocalised and spread out over the whole ring. Delocalised means not attached to a particular atom.

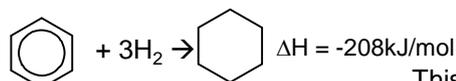
Benzene is a **planar** molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond.

The H-C-C bond angle is 120° in Benzene.

Enthalpies of Hydrogenation



Non delocalised structure

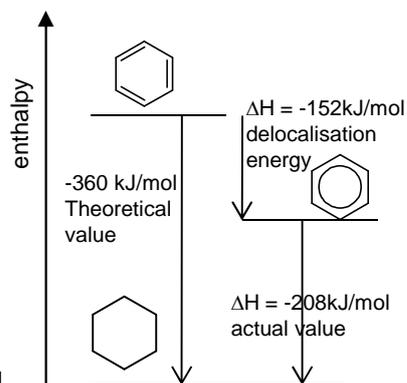


delocalised structure

Theoretically because there are 3 double bonds one might expect the amount of energy to be 3 times as much.

However, the real amount of energy is less. The 6 pi electrons are delocalised and not arranged in 3 double bonds.

This when represented on an energy level diagram shows that the delocalised benzene is more thermodynamically stable.



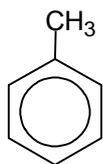
The increase in stability connected to delocalisation is called the **delocalisation energy**.

Reactions of Benzene

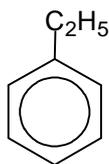
Benzene does not generally undergo addition reactions because these would involve breaking up the delocalised system. Most of Benzene's reactions involve substituting one H for another atom or group of atoms. Benzene has a high electron density and so attracts electrophiles. Its reactions are usually **electrophilic substitutions**.

Naming aromatic molecules

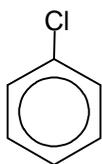
Naming aromatic compounds can be complicated. The simplest molecules are derivatives of benzene and have benzene at the root of the name



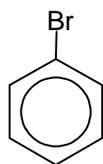
Methylbenzene



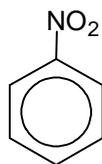
ethylbenzene



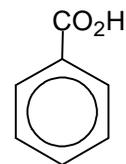
chlorobenzene



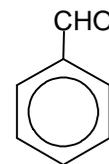
bromobenzene



nitrobenzene

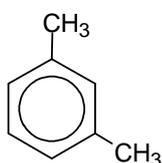


benzenecarboxylic acid

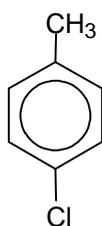


benzaldehyde

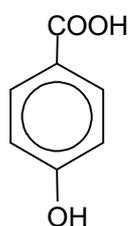
If two or more substituents are present on the benzene ring, their positions must be indicated by the use of numbers. This should be done to give the lowest possible numbers to the substituents. When two or more different substituents are present, they are listed in alphabetical order and di, tri prefixes should be used.



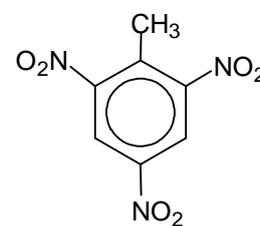
1,3-dimethylbenzene



1-chloro-4-methylbenzene

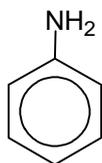


4-hydroxybenzenecarboxylic acid

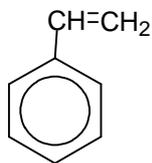


2,4,6-trinitrotoluene

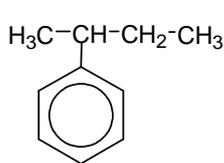
In other molecules the benzene ring can be regarded as a substituent side group on another molecule, like alkyl groups are. The C_6H_5 - group is known as the **phenyl** group.



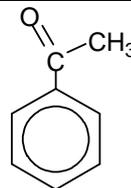
phenylamine



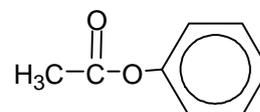
phenylethene



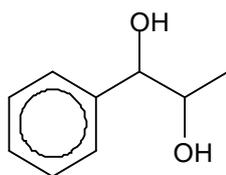
2-phenylbutane



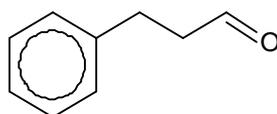
phenylethanone



phenylethanoate



1-phenylpropane-1,2-diol



3-phenylpropanal

Toxicity of Benzene

Benzene is a carcinogen (cancers causing molecule) and is banned for use in schools.

Methylbenzene is less toxic and also reacts more readily than benzene as the methyl side group releases electrons into the delocalised system making it more attractive to electrophiles.

Reactions of Benzene

Combustion

Benzene + oxygen → carbon dioxide + water
 $C_6H_6(l) + 7.5 O_2 \rightarrow 6 CO_2 + 3 H_2O$

Benzene will combust with a very sooty flame. The lower the carbon to hydrogen ratio the sootier the flame.

Halogenation of Benzene

Change in functional group: benzene → bromobenzene

Reagents: Bromine

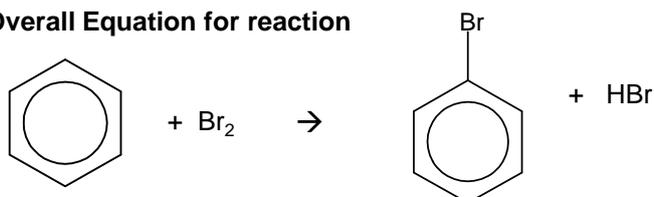
Conditions: Iron(III) bromide catalyst $FeBr_3$

Mechanism: Electrophilic substitution

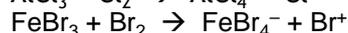
This reaction can be done with chlorine. The catalyst can be $AlCl_3$ or $FeCl_3$

It is possible to create the iron(III) bromide in situ by reacting iron with bromine

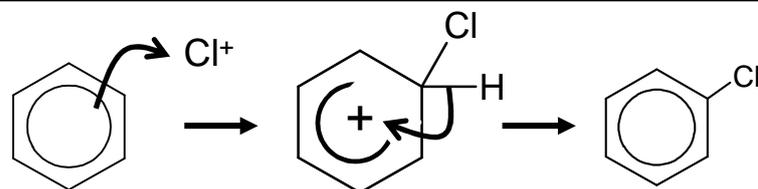
Overall Equation for reaction



Equation for Formation of electrophiles: (Learn!)



Mechanism



The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ catalyst and HCl .



Nitration of Benzene

Change in functional group: benzene → nitrobenzene

Reagents: conc nitric acid in the presence of concentrated sulfuric acid (catalyst)

Mechanism: Electrophilic Substitution

Electrophile: NO_2^+

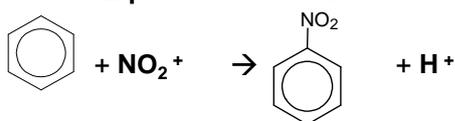
Importance of this reaction

Nitration of benzene and other arenes is an important step in synthesising useful compounds

e.g. explosive manufacture (like TNT, trinitrotoluene/ 2,4,6-trinitromethylbenzene)

and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered in the amines section.)

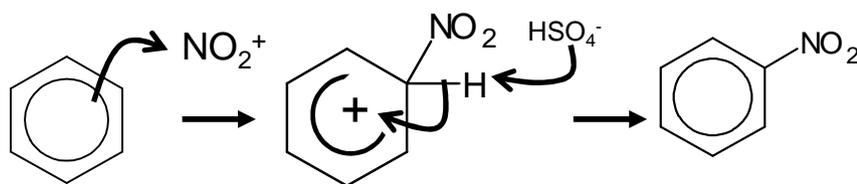
Overall Equation for reaction



Equation for Formation of electrophile: (Learn!)

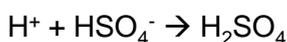


Mechanism



The horseshoe shape of the intermediate must not extend beyond C's 2 to 6

The H^+ ion rejoins with the HSO_4^- to reform H_2SO_4 catalyst.



This reaction is done at $60^\circ C$. On using higher temperatures a second nitro group can be substituted onto different positions on the ring

If the benzene ring already has a side group e.g. methyl then the Nitro group can also join on different positions. A-level does not require knowledge of what positions the groups go on.

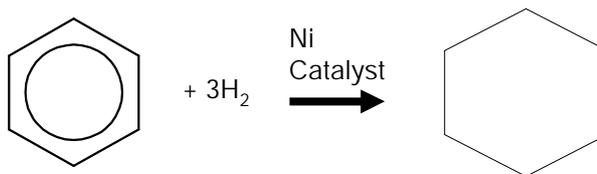
Hydrogenation of Benzene

Reaction: benzene \rightarrow cyclohexane

Reagents: Hydrogen

Conditions: Nickel catalyst at 200C and 30 atm

Type of reaction: Addition and reduction



Friedel Crafts Alkylation

Change in functional group: benzene \rightarrow alkylbenzene

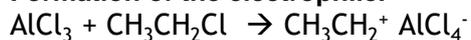
Reagents: chloroalkane in the presence of anhydrous aluminium chloride catalyst

Conditions: heat under reflux

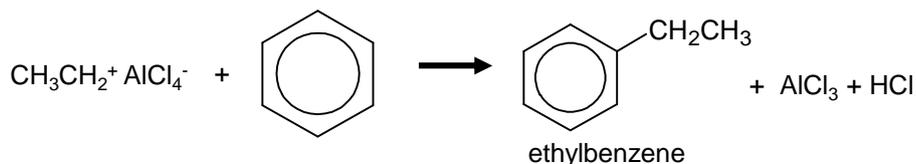
Mechanism: Electrophilic Substitution

Any chloroalkane can be used RCl where R is any alkyl group Eg -CH₃, -C₂H₅. The electrophile is the R⁺.

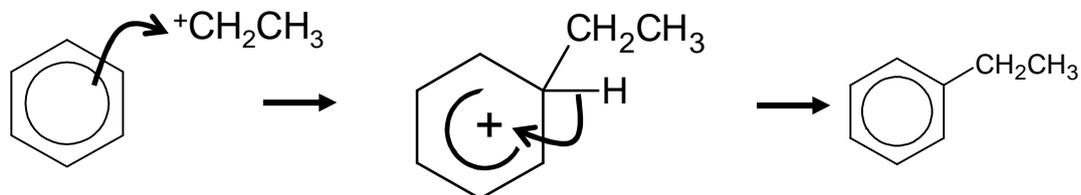
Formation of the electrophile.



Overall Equation for reaction



Mechanism



The H⁺ ion reacts with the AlCl₄⁻ to reform AlCl₃ catalyst and HCl.

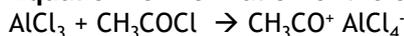


Friedel Crafts Acylation

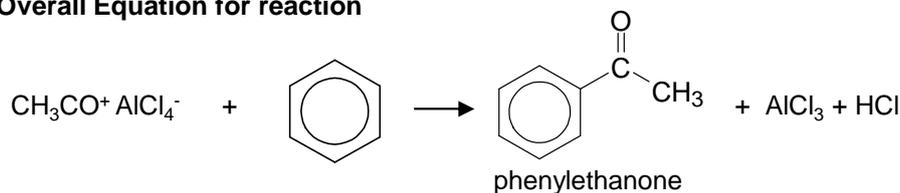
Change in functional group: benzene → phenyl ketone
Reagents: acyl chloride in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux (50°C)
Mechanism: Electrophilic substitution

Any acyl chloride can be used RCOCl where R is any alkyl group e.g. -CH₃, -C₂H₅. The electrophile is the RCO⁺.

Equation for Formation of the electrophile.

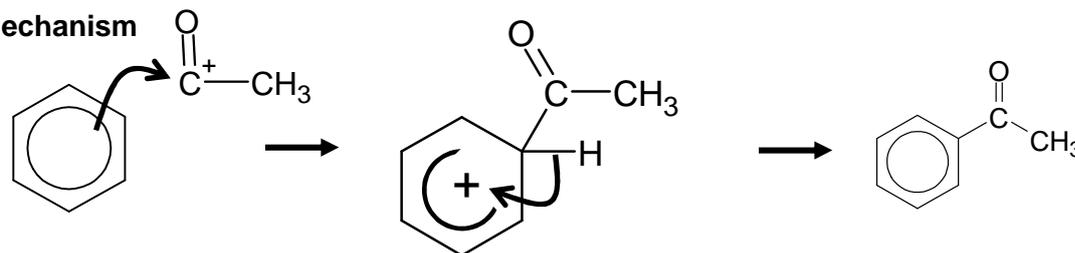


Overall Equation for reaction



These are important reactions in organic synthesis because they introduce a reactive functional group on to the benzene ring

Mechanism



The H⁺ ion reacts with the AlCl₄⁻ to reform AlCl₃ catalyst and HCl.

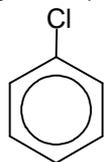


Effect of side groups on benzene ring

Electron releasing side groups such as alkyl groups, phenols and amines releases electrons into the delocalised system making a higher electron density in the ring and it more attractive to electrophiles. They will therefore carry out the substitution reactions more readily with milder conditions.

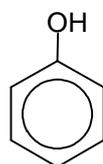
Effect of delocalisation on side groups with lone pairs

If a -OH group, a Cl atom or an NH₂ group is directly attached to a benzene ring the delocalisation in the benzene ring will extend to include the lone pairs on the N, O and Cl. This changes the properties and reactions of the side group.



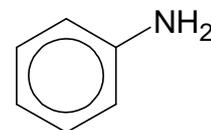
chlorobenzene

The C-Cl bond is made stronger. Typical halogenoalkane substitution and elimination reactions do not occur. Also the electron rich benzene ring will repel nucleophiles



phenol

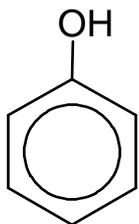
Delocalisation makes the C-O bond stronger and the O-H bond weaker. Phenol does not act like an alcohol- it is more acidic and does not oxidise



phenylamine

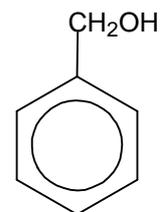
Less basic than aliphatic amines as lone pair is delocalised and less available for accepting a proton

Phenols



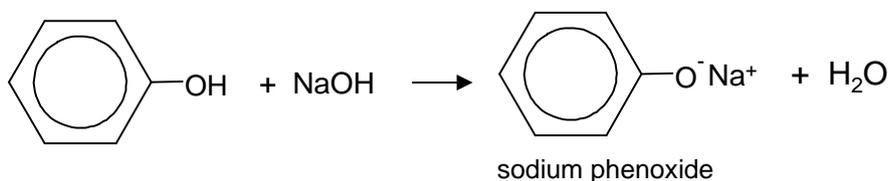
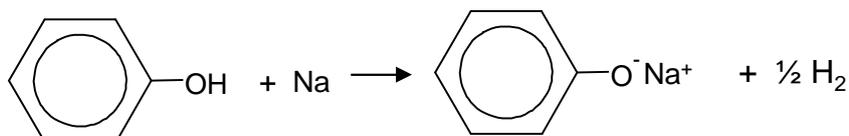
In a phenol the OH group is directly attached to the benzene ring.

In a phenol the lone pair of electrons on the oxygen is delocalised with the electron charge cloud of the arene ring. The delocalised bonding changes the reactivity of the OH group and the arene ring.



This is not a phenol, but is an alcohol because the OH group is attached to an alkyl group rather than the benzene ring.

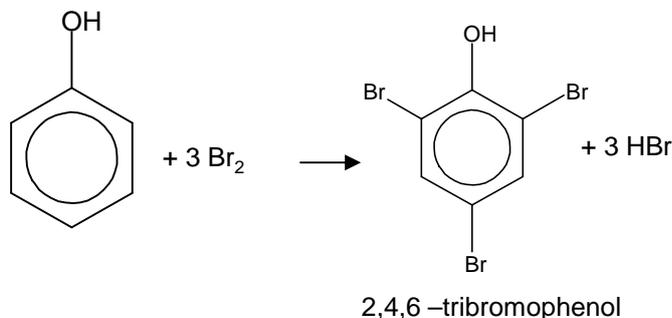
Phenols are very weakly acidic. They are weaker acids than carboxylic acids. Both phenols and carboxylic acids will react with sodium metal and sodium hydroxide. Only carboxylic acids will react with sodium carbonate as a phenol is not strong enough an acid to react.



The sodium phenoxide compound is more soluble than the original phenol. So solid phenol dissolves on addition of NaOH solution.

Reaction of Phenol with Bromine

Reagents: Bromine water
Conditions: room temp



Comparison with benzene

Phenol does not need a FeBr_3 catalyst like benzene and undergoes multiple substitution whereas benzene will only add one Br.

The product in this reaction is a white solid.

In phenol the lone pair of electrons on the oxygen (p-orbital) is partially **delocalised** into the ring. The electron density in the ring increases and the Br_2 is more polarised.

Phenols are used in the production of plastics, antiseptics, disinfectants and resins for paints.

18B. Amines, Amides and Amino Acids

Naming

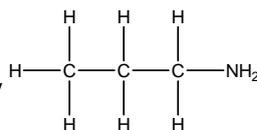
Amines

These end in **-amine**.

There is, however, rather confusingly two ways of using this suffix.

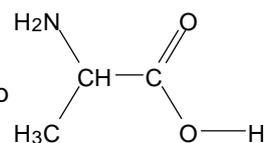
The exam board tend to use the common version where the name stem ends in **-yl** propylamine.

The IUPAC version of the same chemical is propan-1-amine. (This is used in the same way as naming alcohols)



propylamine
Or propan-1-amine

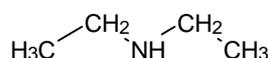
If there is another priority functional group as well as the amine group then the prefix amino is used.



2-aminopropanoic acid.

If the amine is secondary and has two alkyl groups attached to the nitrogen, then each chain is named and the smaller alkyl group is preceded by an **-N** which plays the same role as a number in positioning a side alkyl chain

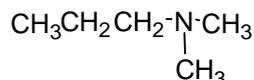
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$
N-methylpropylamine (common name)
N-methylpropan-1-amine (IUPAC name)



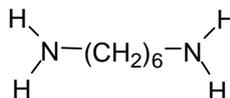
In the common naming version if the chain lengths are the same an **-N** is not used

Diethylamine (common name- does not use N if chains are same length)
N-ethylethanamine (IUPAC name does still use N)

If a tertiary amine similar rules apply, and each alkyl side group is given an **N**



N,N-dimethylpropylamine (common name)
N,N-dimethylpropan-1-amine (IUPAC name)

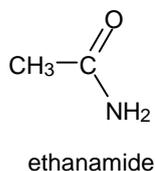


It could also be named
1,6-diaminohexane

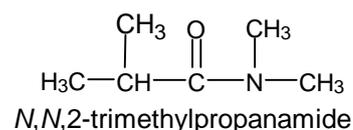
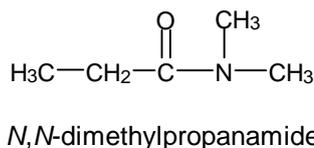
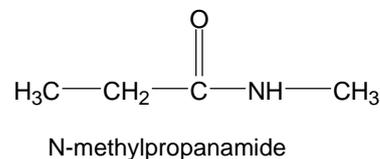
hexane-1,6-diamine

Amides

Add **-amide** to the stem name



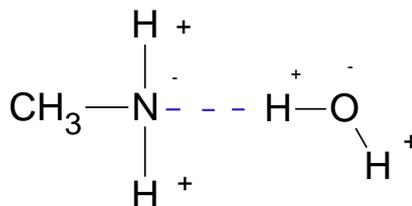
Secondary and tertiary amides are named differently to show the two (or three) carbon chains. The smaller alkyl group is preceded by an **-N** which plays the same role as a number in positioning a side alkyl chain



Properties of Amines

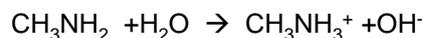
Amines have a characteristic fishy smell

Small amines can form hydrogen bonds with water and therefore can dissolve readily in water.

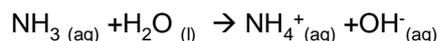


Base Properties

Primary aliphatic amines act as Bronsted-Lowry Bases because the lone pair of electrons on the nitrogen is readily available for forming a dative covalent bond with a H^+ and so accepting a proton.



Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and so make it a stronger base.

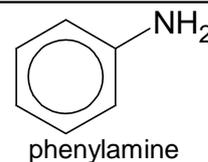


Secondary amines are stronger bases than primary amines because they have more alkyl groups that are substituted onto the N atom in place of H atoms. Therefore more electron density is pushed onto the N atom (as the inductive effect of alkyl groups is greater than that of H atoms).

One might expect using the same trend that tertiary amine would be the strongest amine base but the trend does not hold. The tertiary amines and corresponding ammonium salts are less soluble in water and this makes them less strong bases than the secondary amines. (This point will not be examined)

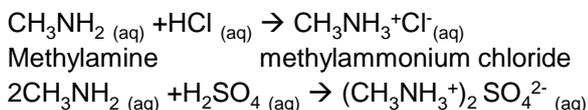
Base strength of aromatic amines

Primary aromatic amines such as phenylamine do not form basic solutions because the lone pair of electrons on the nitrogen delocalise with the ring of electrons in the benzene ring. This means the N is less able to accept protons.



Reactions with acids

Amines as bases react with acids to form ammonium salts.



Addition of NaOH to an ammonium salt will convert it back to the amine

The ionic salts formed in this reaction means that the compounds are soluble in the acid.
e.g. Phenylamine is not very soluble in water but phenylammonium chloride is soluble.

These ionic salts will be solid crystals, if the water is evaporated, because of the strong ionic interactions.

Making a basic buffer from an amine

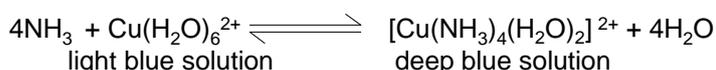
Basic buffers can be made from combining a weak base with a salt of that weak base
e.g. Ammonia and ammonium chloride
Methylamine and methylammonium chloride
Ethylamine and ethylammonium chloride

Formation of complex ions

The lone pair of electrons on the nitrogen enable amines to act as ligands and form dative covalent bonds into transition metal ions to form coloured complex ions.

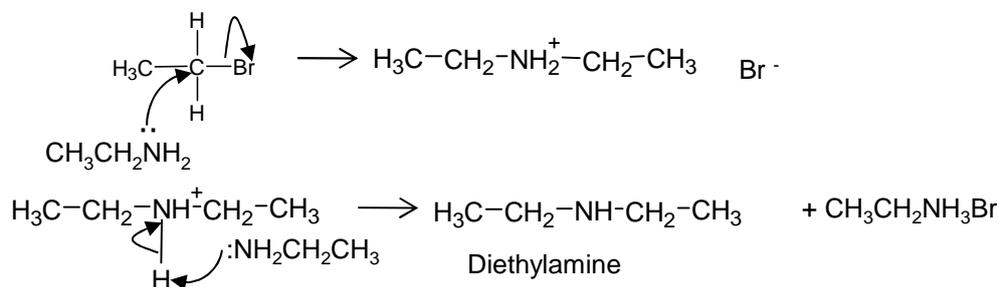
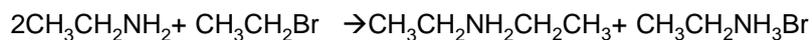


This is a similar ligand exchange reaction to the one where ammonia acts as the ligand.



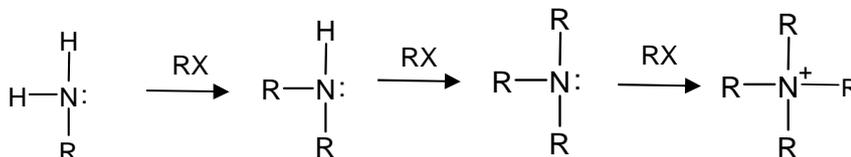
Reaction of primary amines with halogenoalkanes forming secondary amines

Amines will react with halogenoalkanes in a similar way to the reaction of ammonia with halogenoalkanes via a nucleophilic substitution reaction.



The secondary amine formed can also then react with more halogenoalkane to form a tertiary amine and subsequently on to what is called a quaternary ammonium salt

Where RX is the halogenoalkane

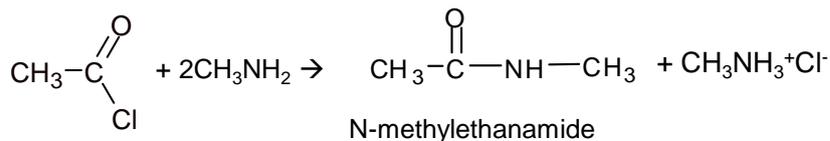


Reaction with primary amines with acyl chlorides

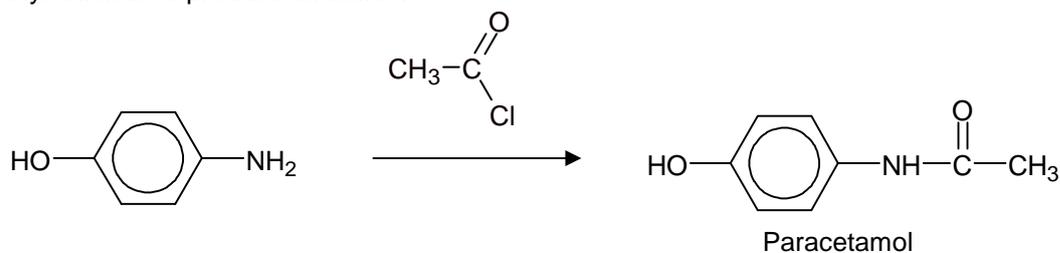
Change in functional group: **acyl chloride** \rightarrow **secondary amide**

Reagent: **primary amine**

Conditions: **room temp.**



Paracetamol is made by the reaction of an aromatic amine with an acyl chloride to produce an amide.

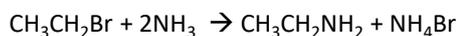


The preparation of primary aliphatic amines

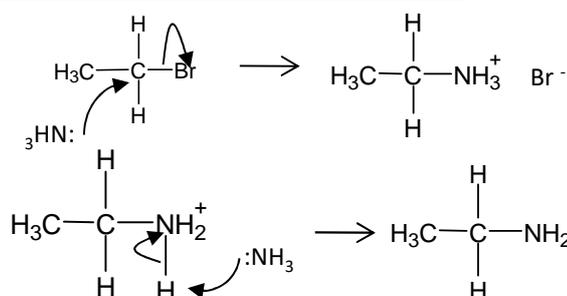
1. Forming a primary amine in a one step reaction of halogenoalkanes with ammonia

Primary amines can be formed by the **nucleophilic substitution** reaction between halogenoalkanes and ammonia in a **one step reaction**. However, as the lone pair of electrons is still available on the N in the amine formed, the primary amine can react in the same nucleophilic way in a successive series of reactions forming secondary, tertiary amines and quaternary ammonium salts.

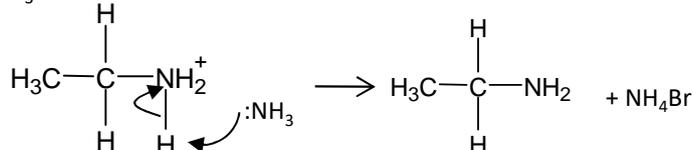
This is therefore not a good method for making a primary amine because of the further reactions. It would mean the desired product would have to be separated from the other products.



Ammonia dissolved in ethanol is the initial nucleophile



In the first step of the mechanism the nucleophile attacks the halogenoalkane to form an intermediate.



In the second step of the mechanism a second ammonia removes a proton from the intermediate (acts as base) to form the amine.

Using an **excess of ammonia** can limit the further subsequent reactions and will **maximise the amount of primary amine** formed.

2. Preparing Amines from Nitriles

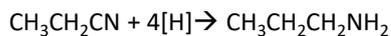
Using the method above of reacting halogenoalkanes and ammonia is not an efficient method for preparing a high yield of the primary amine because of the further substitution reactions that occur.

A better method is to use the following two reactions.

Step 1. convert **halogenoalkane to nitrile** by using KCN in ethanol (heat under reflux)



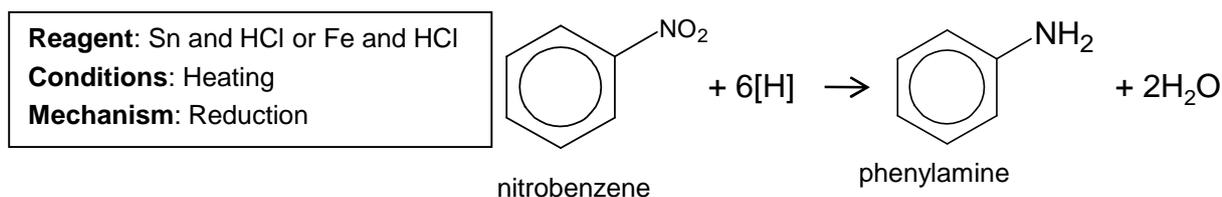
Step 2. reduce **nitrile to amine** by using **LiAlH₄ in ether** or by reducing with H₂ using a Ni catalyst.



A disadvantage of this method is that it is a two step reaction that may therefore have a low yield. Also KCN is toxic.

Reducing nitroarenes to aromatic amines

The nitro group on an arene can be reduced an amine group as follows

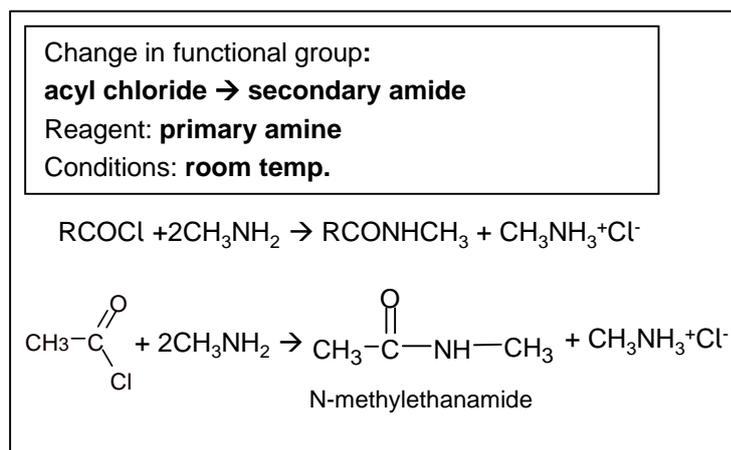


As the reaction is carried out in HCl the salt $C_6H_5NH_3^+Cl^-$ will be formed. Reacting this salt with NaOH will give phenylamine.

The phenylamine formed in this reaction is best separated from the reaction mixture by steam distillation.

Forming Amides

Aliphatic amines and phenylamine can react with acyl chlorides to form amides in a nucleophilic addition-elimination reaction- see chapter 17C for more details.



Condensation Polymerisation

The two most common **types** of condensation polymers are **polyesters** and **polyamides** which involve the formation of an **ester** linkage or an **amide** linkage.

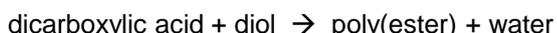
In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g. H₂O or HCl.

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di carboxylic acid, diol, diacyl chloride.

Forming polyesters and polyamide uses these reactions we met earlier in the course

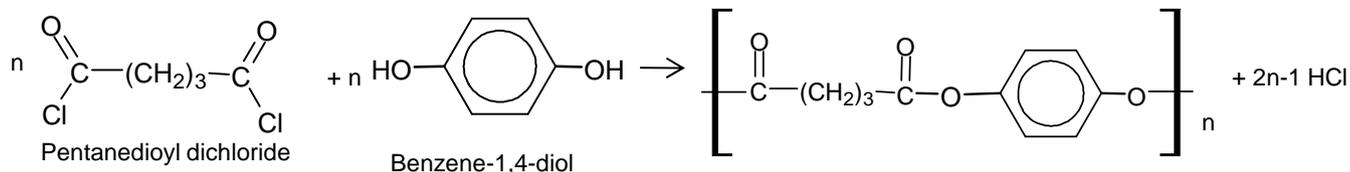
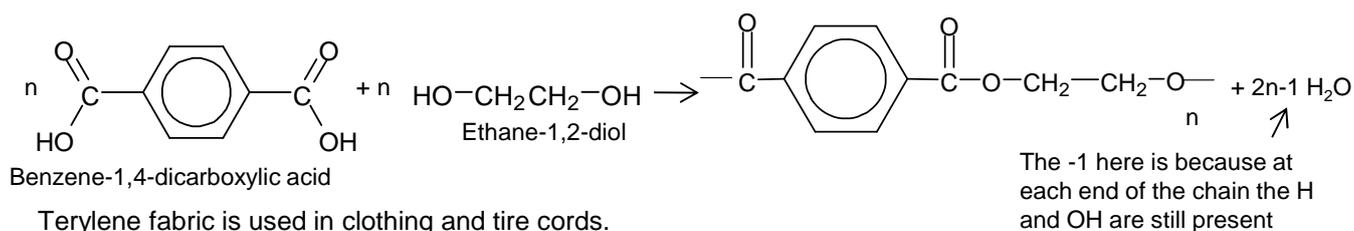


If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:

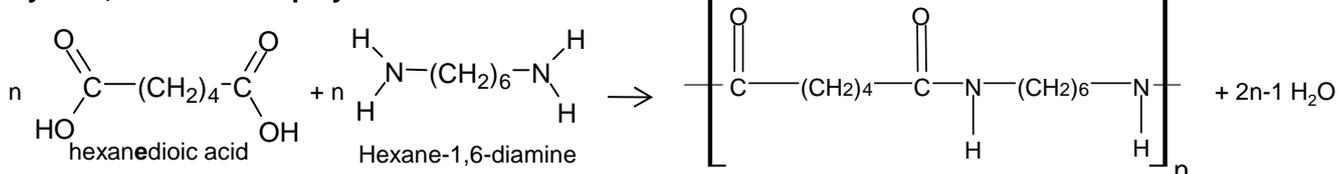


Using the carboxylic acid to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous HCl fumes.

Terylene- a common polyester

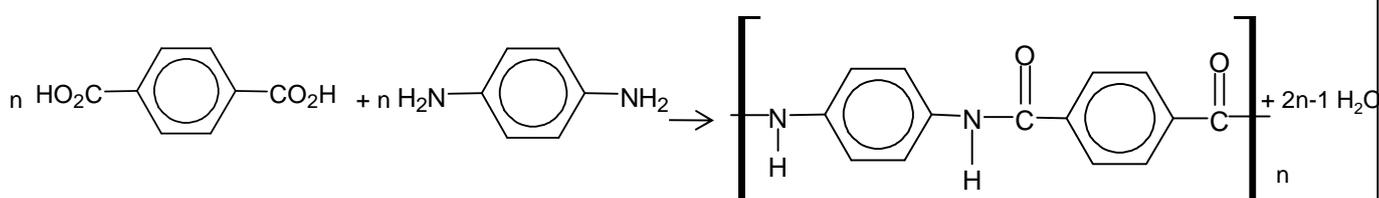


Nylon 6,6 - a common polyamide



The 6,6 stands for 6 carbons in each of the monomers. Different length carbon chains produce different polyamides

Kevlar- a common polyamide

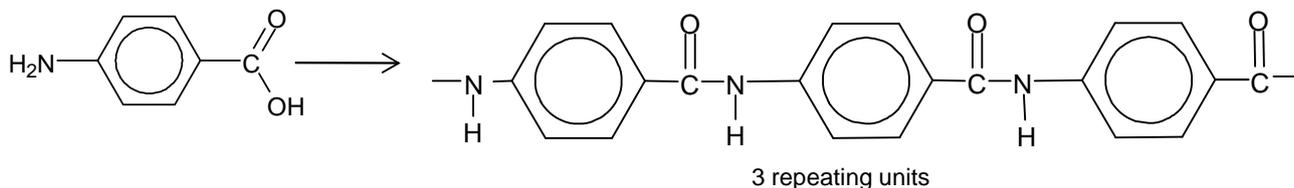
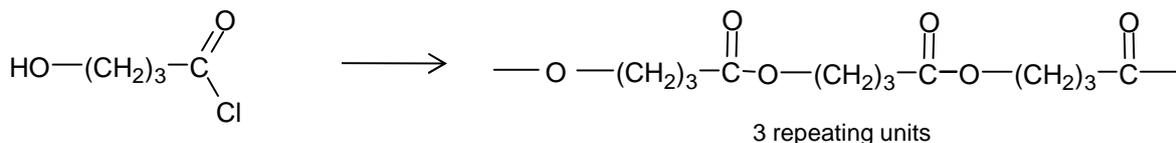


Note on classification for condensation polymers

If asked for **type of polymer**: It is polyamide or polyester

Whereas **type of polymerisation** is **condensation**

It is also possible for polyamides and polyesters to form from **one** monomer, if that monomer contains both the functional groups needed to react



Chemical reactivity of condensation polymers

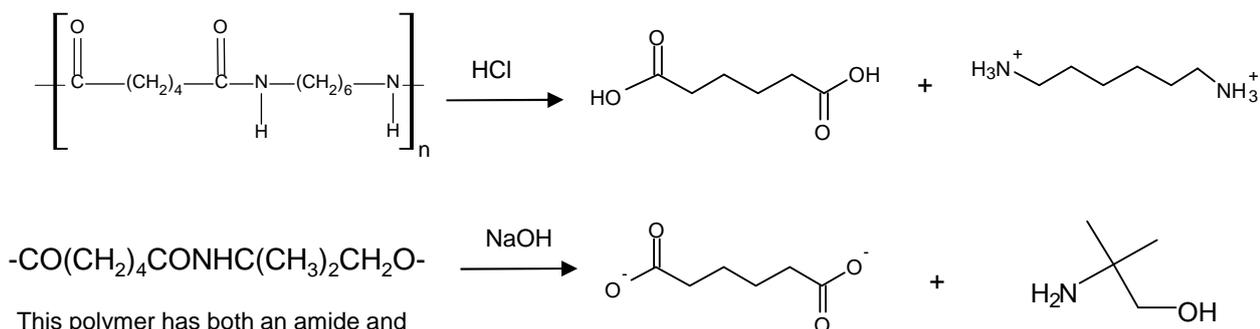
polyesters and polyamides can be broken down by **hydrolysis** and are, therefore, biodegradable

The reactivity can be explained by the presence of **polar bonds** which can attract attacking species such as nucleophiles and acids

Hydrolysis

Polyesters and polyamides can be hydrolysed by acid and alkali

The hydrolysis will result in the original monomers forming- although the carboxylic acid or amine group will be in salt form depending on whether the conditions are alkaline or acidic



This polymer has both an amide and ester link

Intermolecular bonding between condensation polymers chains

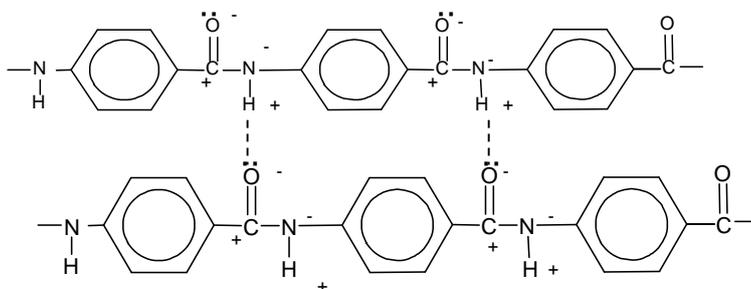
Polyesters have permanent dipole forces between the C⁺=O⁻ groups in the different chains in addition to the London forces between the chains.

Polyamides (and proteins) have **hydrogen bonding** between the lone pairs on oxygen in C⁺=O⁻ groups and the H in the N⁻-H⁺ groups in the different chains.

There are also **Permanent dipole-permanent dipole forces** because the polar C=O bond and polar C-N bond

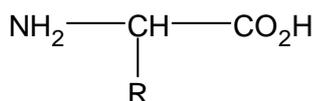
There are also **London forces** which are large because there are many electrons in the molecule

Polyamides will therefore have higher melting points than polyesters.



Amino Acids

General structure of an amino acid

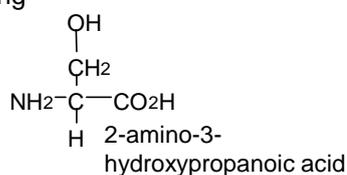
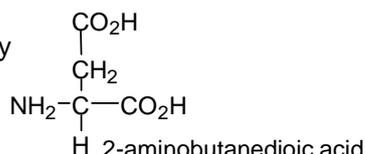
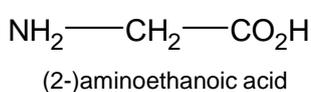


The R group can be a variety of different things depending on what amino acid it is.

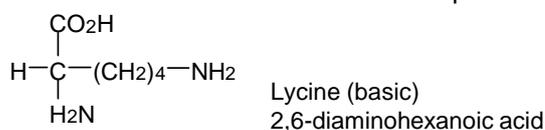
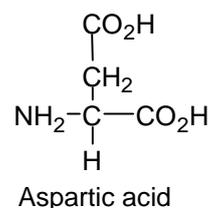
The simplest amino acid is glycine, where the R is an H $\text{NH}_2 - \text{CH}_2 - \text{CO}_2\text{H}$

Naming amino acids

You do not need to know any common names for the 20 essential amino acids. We should, however, be able to name given amino acids using IUPAC organic naming



Some amino acids have an extra carboxylic acid or an amine group on the R group. These are classed as acidic or basic (respectively) amino acids

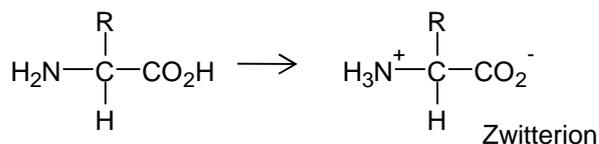


Zwitterions

The no charge form of an amino acid never occurs. The amino acid exists as a dipolar zwitterion.

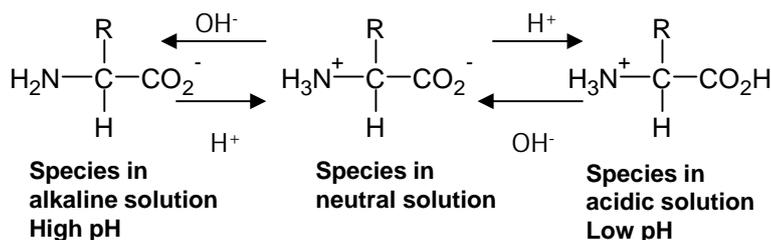
Amino acids are often **solids**

The **ionic interaction** between zwitterions explains the relatively high melting points of amino acids as opposed to the weaker hydrogen bonding that would occur in the no charge form.

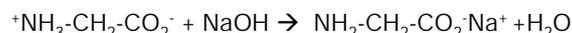
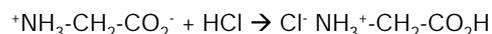


Acidity and Basicity

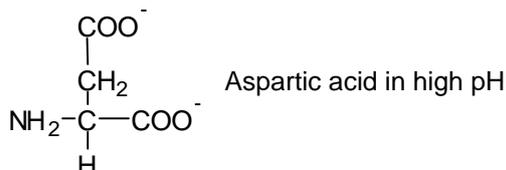
The amine group is basic and the carboxylic acid group is acidic.



Amino acids act as weak buffers and will only gradually change pH if small amounts of acid or alkali are added to the amino acids.



The extra carboxylic acid or amine groups on the R group will also react and change form in alkaline and acid conditions



Chromatography of Amino Acids

A mixture of amino acids can be separated by chromatography and identified from the amount they have moved.

$$R_f \text{ value} = \frac{\text{distance moved by amino acid}}{\text{distance moved by the solvent}}$$

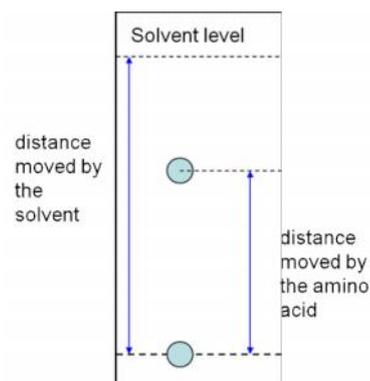
Each amino acid has its own R_f value. Compare an unknown amino acid's R_f value with known values in a data book to identify the amino acid

Method

Take chromatography paper and draw a pencil line 1.5cm from bottom.

With a capillary tube put a small drop of amino acid on pencil line
Roll up paper and stand it in a large beaker.

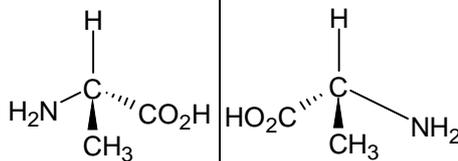
The solvent in the beaker should be below the pencil line.
Allow to stand for 20 mins and mark final solvent level
Spray paper with ninhydrin and put in oven



If ninhydrin is sprayed on an amino acid and then heated for 10 minutes then red to blue spots appear. This is done because amino acids are transparent and cannot be seen.

Optical Activity

All amino acids, except glycine, are chiral because there are four different groups around the C

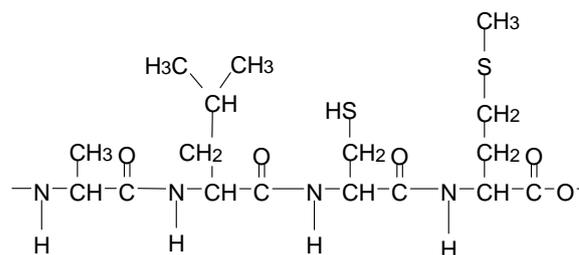
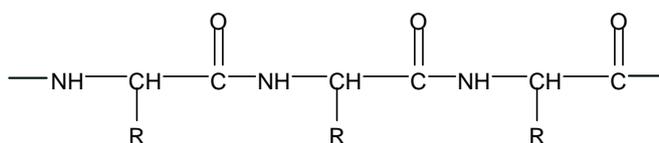


They rotate plane polarised light.

Optical isomers have similar physical and chemical properties, but they rotate plane polarised light in different directions.

Proteins

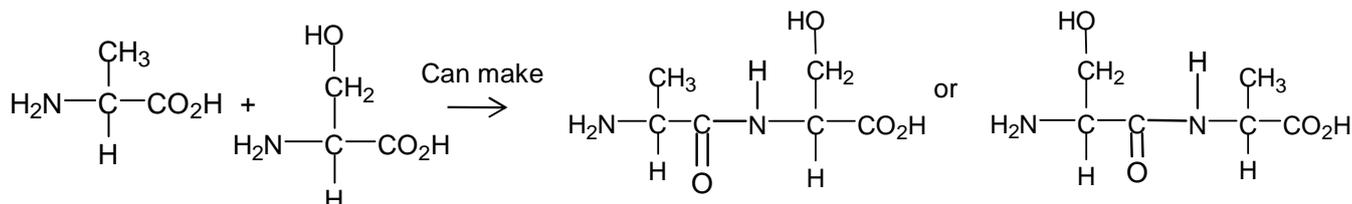
Proteins are polymers made from combinations of amino acids. The amino acids are linked by peptide links, which are the amide functional group.



Dipeptides

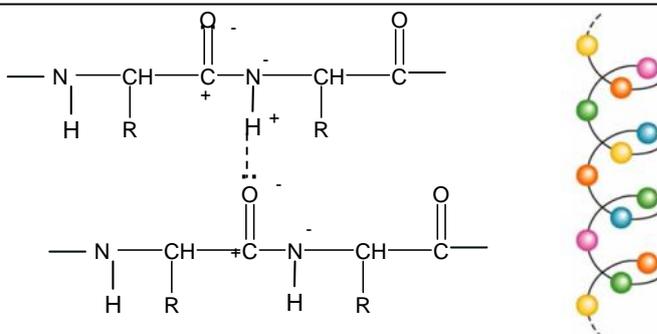
Dipeptides are simple combination molecules of two amino acids with one amide (peptide) link.

For any two different amino acids there are two possible combinations of the amino acids in the dipeptide.



Importance of hydrogen bonding in proteins

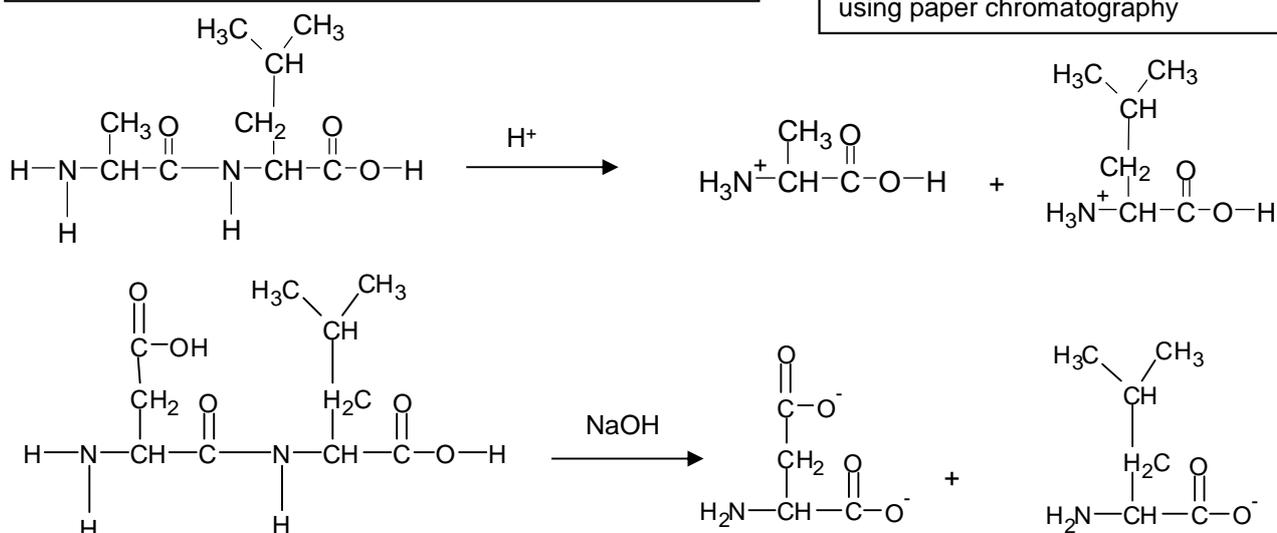
The 3D arrangement of amino acids with the polypeptide chain in a corkscrew shape is held in place by Hydrogen bonds between the H of $-NH^+$ group and the $-O$ of $C=O$.



Hydrolysis of di-peptides/proteins

If proteins are heated with dilute acid or alkali they can be hydrolysed and split back in to their constituent amino acids.

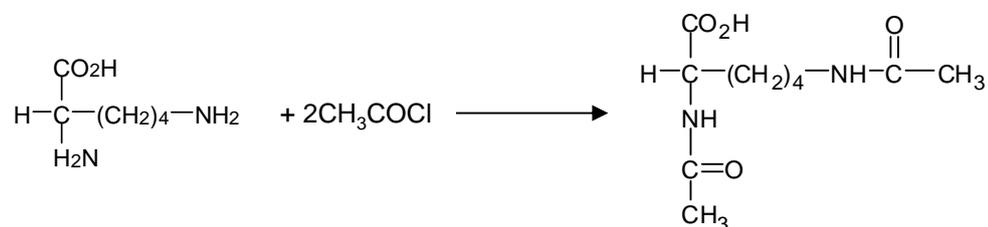
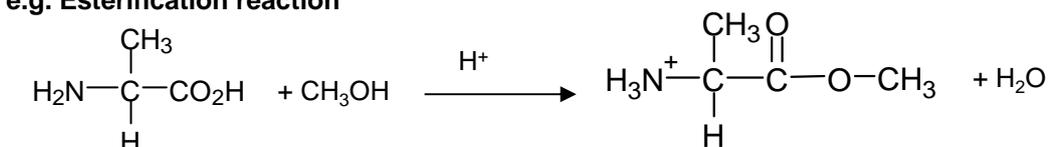
The composition of the protein molecule may then be deduced by using paper chromatography



Other reactions of amino acids

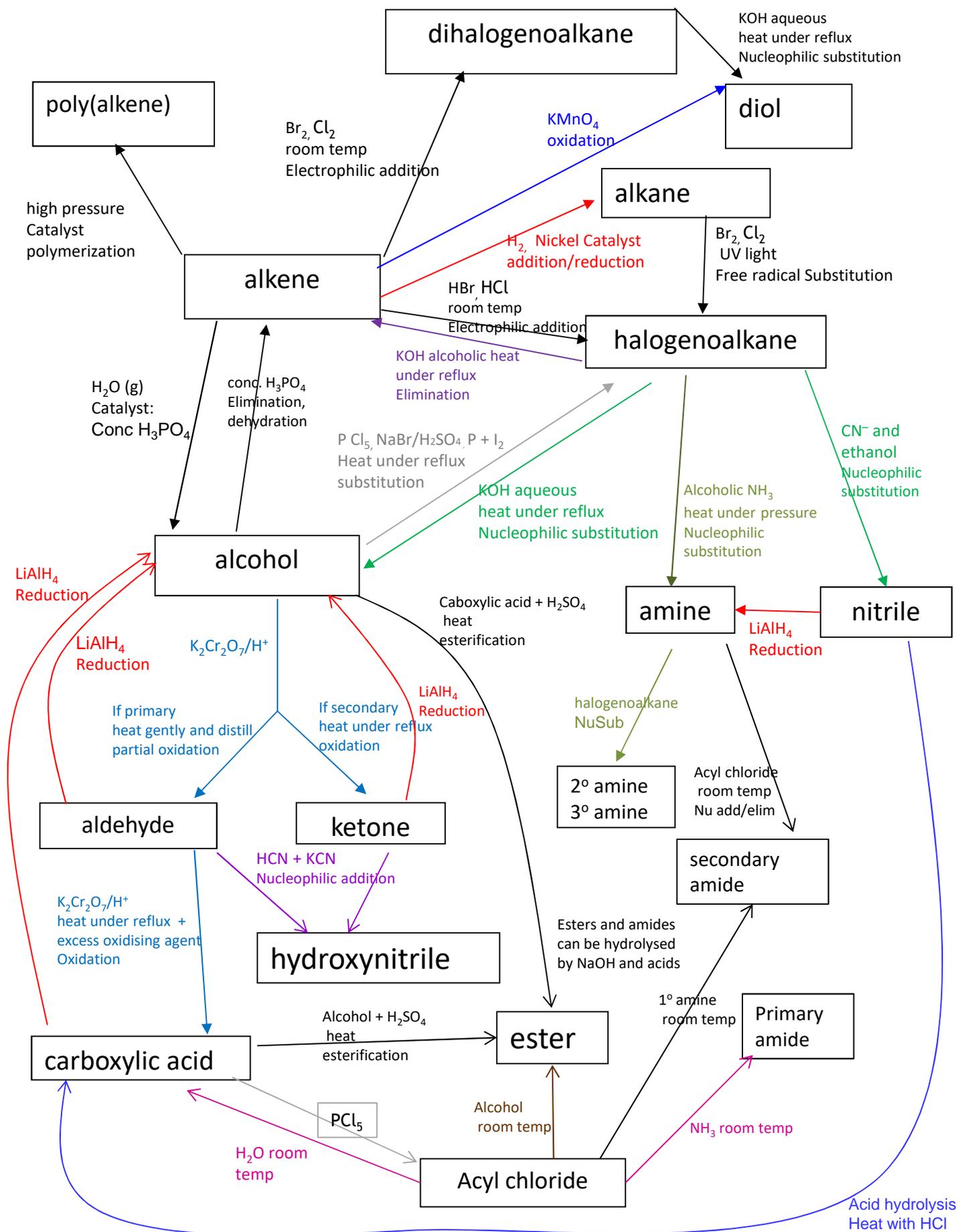
The carboxylic acid group and amine group in amino acids can undergo the usual reactions of these functional groups met in earlier topics. Sometimes questions refer to these.

e.g. Esterification reaction

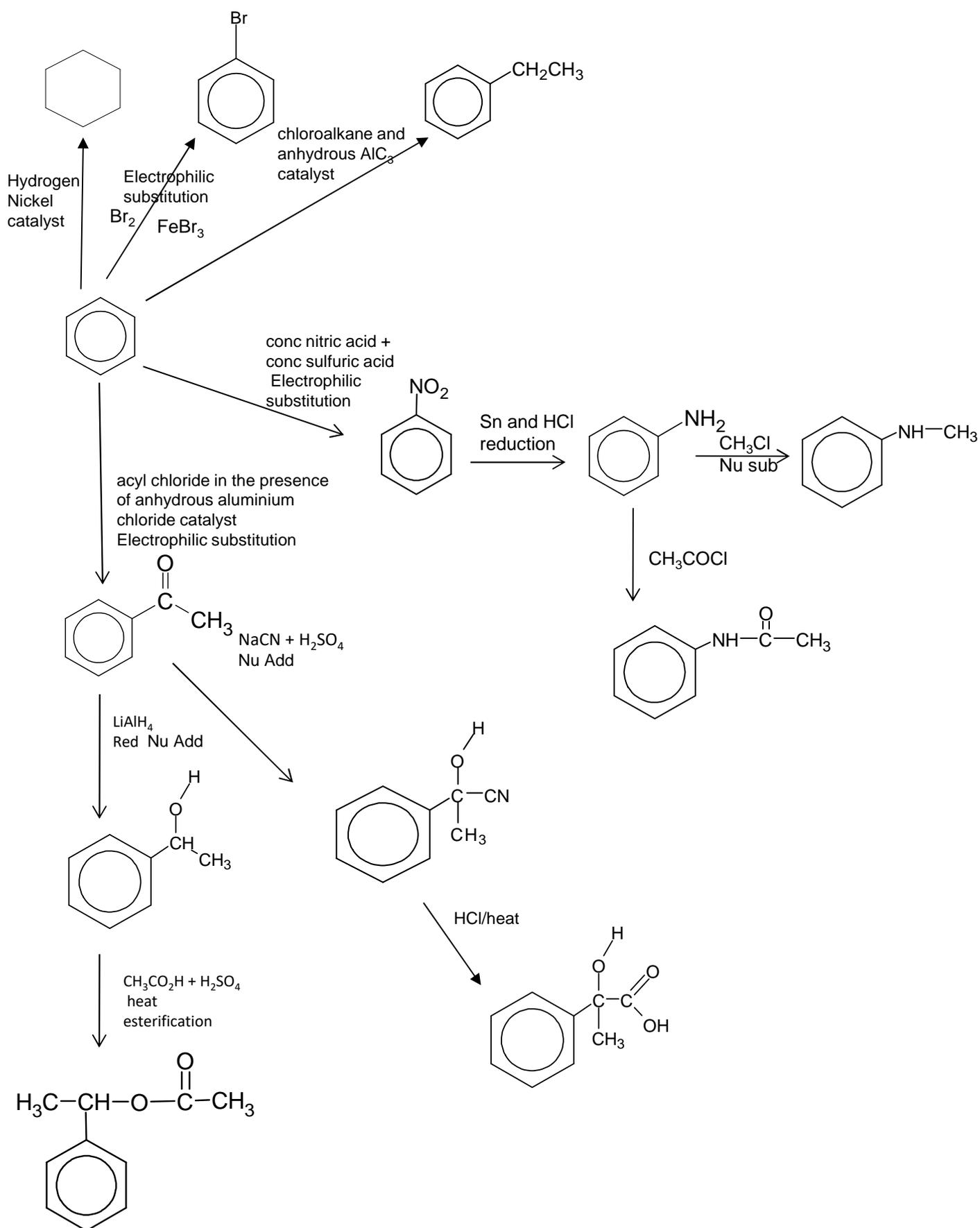


If the R group contains a amine or carboxylic acid then these will do the same reactions as the amine and carboxylic groups

18C. Synthetic Routes



Aromatic synthetic routes

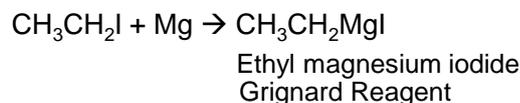


Grignard Reactions

Grignard Reagent is used to increase the length of the carbon chain in a molecule

Preparing Grignard Reagent

A halogenoalkane is dissolved in dry ether and reacted with magnesium to produce the reactive Grignard Reagent

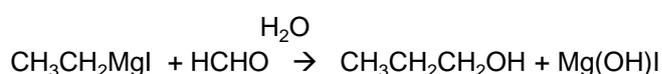


This Grignard reagent is highly reactive and the alkyl group can be considered to have a negative charge. The R⁻ [Mg⁺I] and so contains a nucleophilic carbon atom

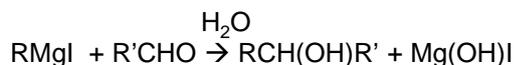
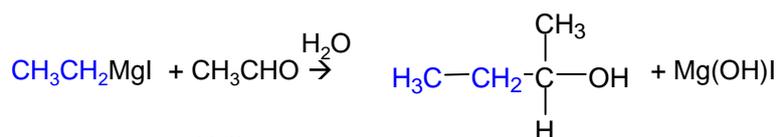
Reactions of Grignard Reagent

Reactions with carbonyls

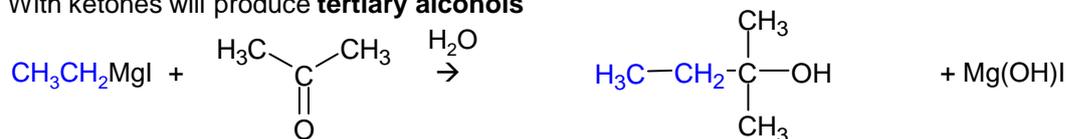
With methanal will produce a **primary alcohol**



With other aldehydes will produce **secondary alcohols**

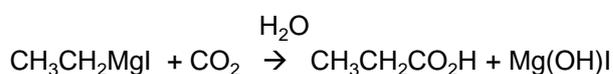


With ketones will produce **tertiary alcohols**



Reaction with carbon dioxide

With CO₂ will produce a **carboxylic acid**



The carbon chain can also be increased by the introduction of a nitrile group into a compound by either reacting a halogenoalkane with KCN (see chapter 6D) or producing hydroxynitriles from carbonyls (see chapter 17B)

Organic techniques

Distillation

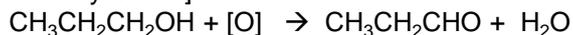
In general used as separation technique to separate an organic product from its reacting mixture. Need to collect the distillate of the approximate boiling point range of the desired liquid.

Classic AS reaction using distillation

Reaction: primary alcohol \rightarrow aldehyde

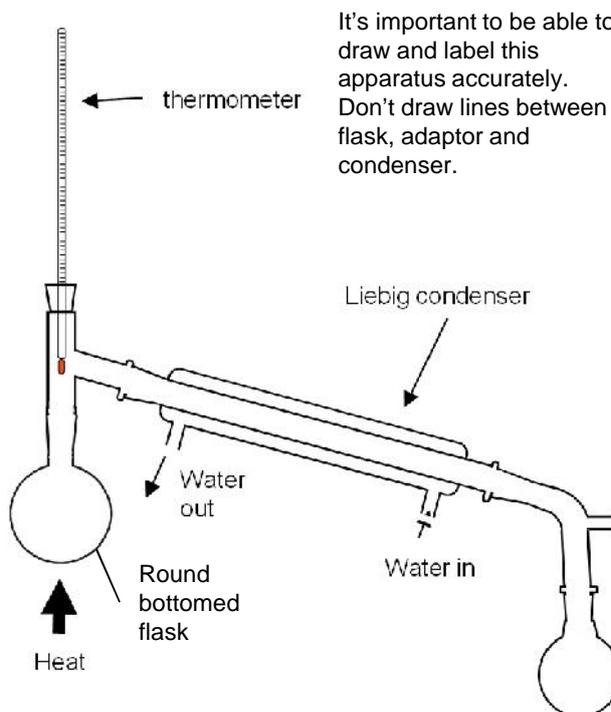
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.

Conditions: use a limited amount of dichromate and **warm gently and distil** out the aldehyde as it forms [This prevents further oxidation to the carboxylic acid]



Observation

Orange dichromate solution changes to green colour of Cr^{3+} ions



It's important to be able to draw and label this apparatus accurately. Don't draw lines between flask, adaptor and condenser.

Reflux

Reflux is used when heating organic reaction mixtures for long periods. The condenser prevents organic vapours from escaping by condensing them back to liquids.

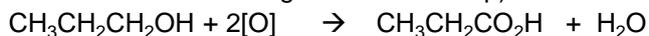
Never seal the end of the condenser as the build up of gas pressure could cause the apparatus to explode. This is true of any apparatus where volatile liquids are heated

Classic AS reaction using reflux

Reaction: primary alcohol \rightarrow carboxylic acid

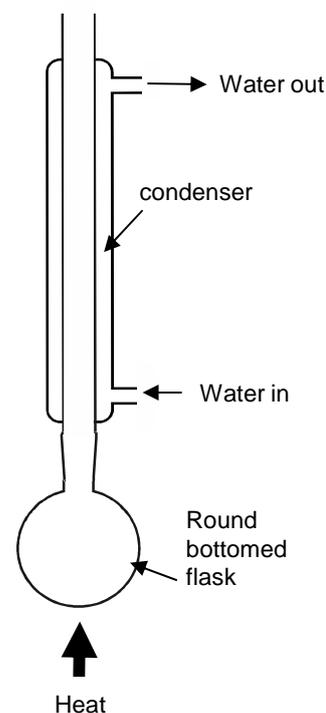
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid

Conditions: use an excess of dichromate, and **heat under reflux:** (distil off product after the reaction has finished using distillation set up)



Observation

Orange dichromate solution changes to green colour of Cr^{3+} ions



Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling by **making small bubbles** form instead of large bubbles

It's important to be able to draw and label this apparatus accurately.

- Don't draw lines between flask and condenser.
- Don't have top of condenser sealed
- Condenser must have outer tube for water that is sealed at top and bottom
- Condenser must have two openings for water in and out that are open

Purifying an organic liquid General method

- Put the distillate of impure product into a separating funnel
- wash product by adding either
 - sodium hydrogencarbonate solution, shaking and releasing the pressure from CO₂ produced.
 - Saturated sodium chloride solution
- Allow the layers to separate in the funnel, and then run and discard the aqueous layer.
- Run the organic layer into a clean, dry conical flask and add three spatula loads of drying agent (e.g. anhydrous sodium sulfate, calcium chloride) to dry the organic liquid. When dry the organic liquid should appear clear.
- Carefully decant the liquid into the distillation flask
- Distill to collect pure product

Sodium hydrogencarbonate will neutralise any remaining reactant acid.

Sodium chloride will help separate the organic layer from the aqueous layer

The layer with lower density will be the upper layer. This is usually the organic layer

The drying agent should

- be insoluble in the organic liquid
- not react with the organic liquid

Decant means carefully pour off organic liquid leaving the drying agent in the conical flask



Separating funnel

Purifying an organic solid: Recrystallisation

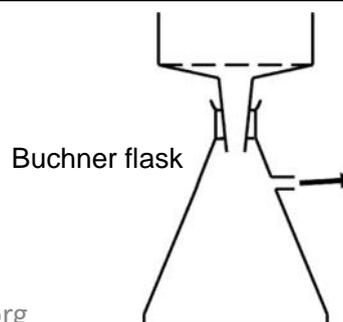
Used for purifying aspirin

Step	Reason
1. Dissolve the impure compound in a minimum volume of hot (near boiling) solvent .	An appropriate solvent is one which will dissolve both compound and impurities when hot and one in which the compound itself does not dissolve well when cold. The minimum volume is used to obtain saturated solution and to enable crystallisation on cooling (If excess (solvent) is used, crystals might not form on cooling)
2. Hot filter solution through (fluted) filter paper quickly.	This step will remove any insoluble impurities and heat will prevent crystals reforming during filtration
3. Cool the filtered solution by inserting beaker in ice	Crystals will reform but soluble impurities will remain in solution form because they are present in small quantities so the solution is not saturated with the impurities. Ice will increase the yield of crystals
4. Suction filtrate with a buchner flask to separate out crystals	The water pump connected to the Buchner flask reduces the pressure and speeds up the filtration.
5 Wash the crystals with distilled water	To remove soluble impurities
6. Dry the crystals between absorbent paper	

Loss of yield in this process

- Crystals lost when filtering or washing
- Some product stays in solution after recrystallisation
- other side reactions occurring

If the crystals are not dried properly the mass will be larger than expected which can lead to a percentage yield >100%

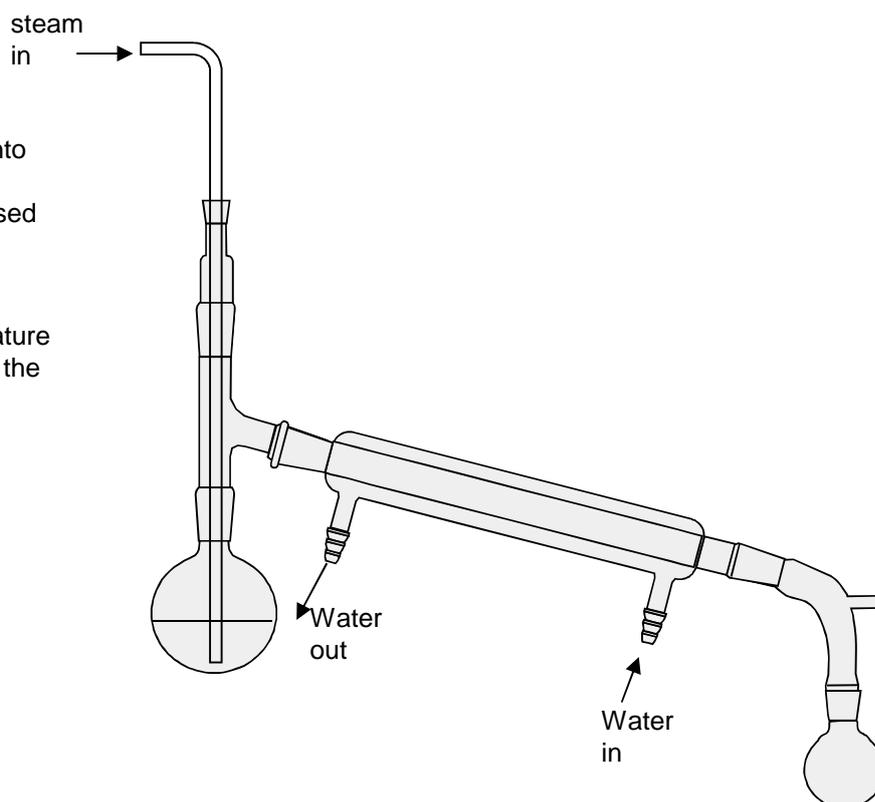


Steam distillation

In steam distillation steam is passed into the mixture and the product vapour is distilled off with the water and condensed

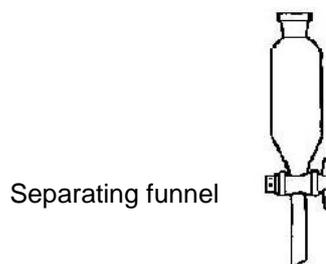
Advantage of steam distillation:

The product distils at a lower temperature which can prevent decomposition of the product if it has a high boiling point



Solvent extraction

Mix organic solvent and oil-water mixture in a separating funnel then separate the oil layer.
Distil to separate oil from organic solvent
Add anhydrous CaCl_2 to clove oil to dry oil
Decant to remove CaCl_2



Safety and hazards

A **hazard** is a substance or procedure that can have the potential to do harm.
Typical hazards are toxic/flammable /harmful/
irritant /corrosive /oxidizing/ carcinogenic

RISK: This is the probability or chance that harm will result from the use of a hazardous substance or a procedure

Irritant - dilute acid and alkalis- wear goggles
Corrosive- stronger acids and alkalis wear goggles
Flammable – keep away from naked flames
Toxic – wear gloves- avoid skin contact- wash hands after use
Oxidising- Keep away from flammable / easily oxidised materials

Hazardous substances in low concentrations or amounts will not pose the same risks as the pure substance.

Measuring melting point

One way of testing for the degree of purity is to determine the melting "point", or melting range, of the sample.

If the sample is very pure then the melting point will be a sharp one, at the same value as quoted in data books.

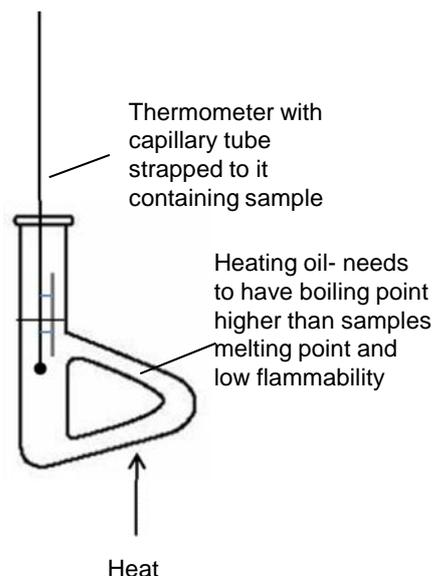
If **impurities** are present (and this can include solvent from the recrystallisation process) the **melting point will be lowered** and the sample will **melt over a range** of several degrees Celsius

Melting point can be measured in an electronic melting point machine or by using a practical set up where the capillary tube is strapped to a thermometer immersed in some heating oil.

In both cases a small amount of the salt is put into a capillary tube.

Comparing an experimentally determined melting point value with one quoted in a data source will verify the degree of purity.

Sometimes an error may occur if the temperature on the thermometer is not the same as the temperature in the actual sample tube.



Measuring boiling point

Purity of liquid can be determined by measuring a boiling point. This can be done in a distillation set up or by simply boiling a tube of the sample in an heating oil bath.

Pressure should be noted as changing pressure can change the boiling point of a liquid

Measuring boiling point is not the most accurate method of identifying a substance as several substances may have the same boiling point.

To get a correct measure of boiling point the thermometer should be above the level of the surface of the boiling liquid and be measuring the temperature of the saturated vapour.

Bringing it all together

1. Work out empirical formula

Elemental analysis C 66.63% H 11.18% O 22.19%

C	H	O
66.63/12	11.18/1	22.19/16
=5.5525	=11.18	=1.386875
=4	=8	=1

2. Using molecular ion peak m/z value from mass spectrum calculate Molecular formula

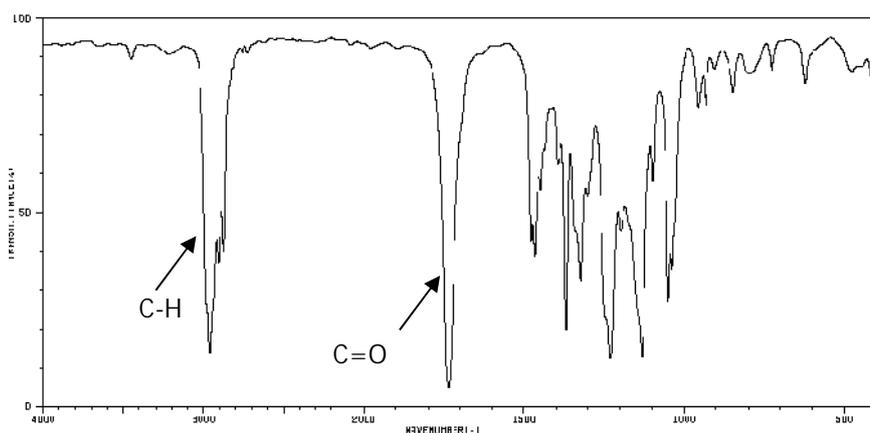
molecular ion peak m/z value= 144

Mr empirical formula $C_4H_8O = 72$

If Mr molecular formula 144 then compound is $C_8H_{16}O_2$

3. Use IR spectra or functional group chemical tests to identify main bonds/functional group

$C_8H_{16}O_2$ could be an ester, carboxylic acid or combination of alcohol and carbonyl. Look for IR spectra for C=O and O-H bonds

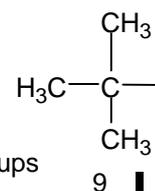


There is a C=O but no O-H absorptions, so must be an ester.

4. Use NMR spectra to give details of carbon chain

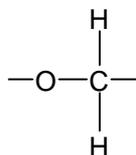
4 peaks – only 4 different environments.

singlet of area 9
At $\delta = 0.9$
Means 3 CH_3 groups



Peak at δ 4 shows H-C-O

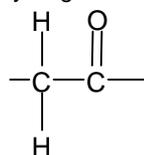
Area 2 suggests CH_2
Quartet means next to a CH_3



2

Peak at δ 2.2 shows H-C=O

Area 2 suggests CH_2
Singlet means adjacent to C with no hydrogens

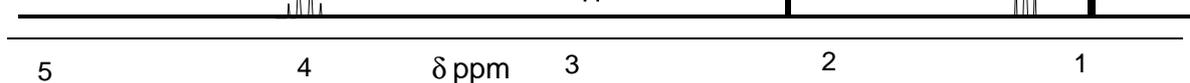


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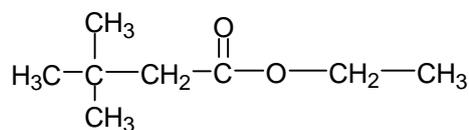
Peak at δ 1.2 shows R- CH_3
Area 3 means CH_3
Triplet means next to a CH_2



3



Put all together to give final structure



Testing for Organic Functional Groups

Functional group	Reagent	Result
Alkene	Bromine water	Orange colour decolourises
Alcohols + carboxylic acids	PCl ₅	Misty fumes of HCl produced
Alcohols, phenols, carboxylic acids	Sodium metal	Effervescence due to H ₂ gas
Carbonyls	2,4-DNP	Orange/red crystals produced
Aldehyde	Fehling's solution	Blue solution to red precipitate
Aldehyde	Tollen's reagent	Silver mirror formed
Carboxylic acid	Sodium carbonate	Effervescence of CO ₂ evolved
1° 2° alcohol and aldehyde	Sodium dichromate and sulfuric acid	Orange to green colour change
chloroalkane	Warm with silver nitrate	Slow formation of white precipitate of AgCl
Acyl chloride	Silver nitrate	Vigorous reaction- steamy fumes of HCl- rapid white precipitate of AgCl

Tollen's Reagent

Reagent: Tollen's Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of [Ag(NH₃)₂]⁺.

Conditions: heat gently

Reaction: **aldehydes only** are oxidised by Tollen's reagent into a carboxylic acid and the silver(I) ions are reduced to silver atoms

Observation: with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.



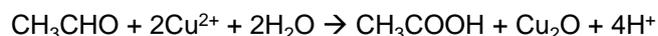
Fehling's solution

Reagent: Fehling's Solution containing blue Cu²⁺ ions.

Conditions: heat gently

Reaction: **aldehydes only** are oxidised by Fehling's Solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide.

Observation: **Aldehydes** :Blue Cu²⁺ ions in solution change to a red precipitate of Cu₂O. **Ketones do not react**



The presence of a carboxylic acid can be tested by addition of **sodium carbonate**. It will fizz and produce carbon dioxide

