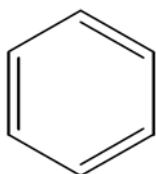


# Chemistry Unit 3 – Rings, Polymers and Analysis

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## 1. Structure of Benzene

**The molecular formula of Benzene  $C_6H_6$  cannot be explained as the structure shown below; it fails to explain the chemical and physical properties of Benzene correctly.**

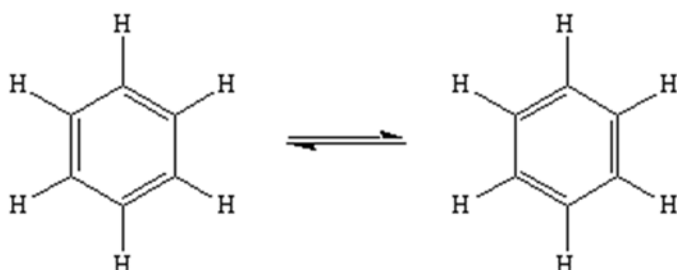


**The model fails to explain Benzene's low reactivity as:**

- **$C=C$  double bonds would react in a similar way to alkenes**
- **They would expect Bromine water to change from orange to colourless.**

**Benzene, however, does not take part in any electrophilic addition reactions as expected.**

**Kekule suggested that Benzene had two forms in rapid equilibrium, shown below.**



**X-rays determined, however, that six carbon-carbon bonds were of the same length, 0.139nm. This suggested his structure was incorrect as  $C=C$  and  $C-C$  bonds are of different lengths.**

**Also, the hydrogenation of Benzene (Cyclohexa-1,3,5-triene) is expected to have an enthalpy change of hydrogenation of  $-360 \text{ kJmol}^{-1}$ . However, it is only  $-208 \text{ kJmol}^{-1}$**

**This means the real structure is more stable and explains why Benzene is less reactive than alkenes, hence why it does not react with Bromine water.**

## 2. Formation of structure of Benzene

The weaknesses in the Kekule model led to development of the delocalised model:

- Benzene is a cyclic hydrocarbon with 6 carbon and 6 hydrogen atoms.
- The 6 C atoms are arranged in a planar hexagonal ring
- The bond angle and shape around each Carbon is 120° Trigonal Planar
- Each C has 4 outer shell electrons.
  - 3 of these bond to two other carbon atoms, and 1 to a hydrogen atom.
  - These form a sigma bond.
  - A fourth outer shell electron in the 2p orbital is left behind above and below the planes of the carbon atoms
- The electron in the p-orbital of a carbon atom overlaps with the electrons in a p-orbital of the carbon atoms on the other side. This results in a ring of electron density above and below the plane of carbon atoms.
- This overlap produces a Pi bond

Due to the delocalisation of the electrons in Benzene, it has increased energetic stability.

## 3. Chemical Reactivity of Benzene

Benzene is more stable than expected- Benzene struggles to take part in addition reactions, and under normal conditions, it does not:

- Decolourise bromine water
- React with strong acids such as HCl
- React with the 3 halogens, Cl, Br or I

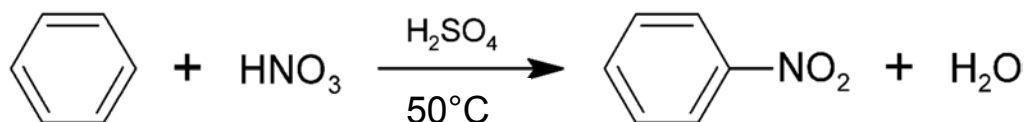
In addition reactions, the electron from the delocalised system would need to bond to the atom or groups of atoms being added.

This would reduce the stability of the product - addition reactions would disrupt the delocalisation of the ring structure.

Benzene, instead, takes part in substitution reactions – this retains the delocalisation and the stability of the benzene ring.

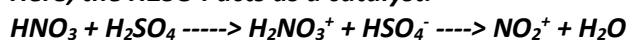
## 4. Nitration of Benzene

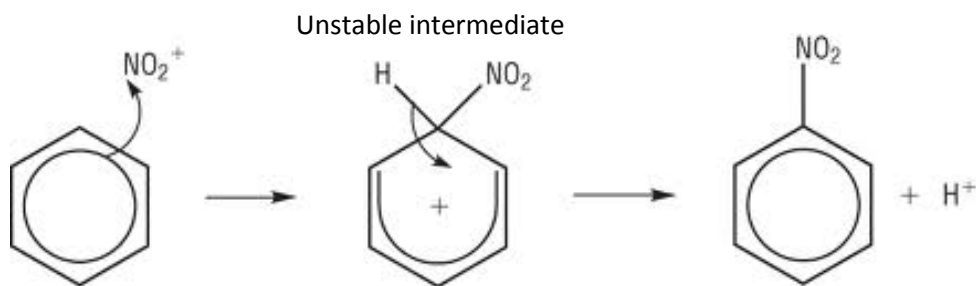
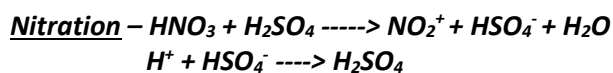
In nitration, one of the hydrogen atoms is replaced by a nitro (NO<sub>2</sub> group)



The benzene is heated gently under reflux – if the heat is too high multiple nitro groups are added to the benzene ring.

Here, the H<sub>2</sub>SO<sub>4</sub> acts as a catalyst.





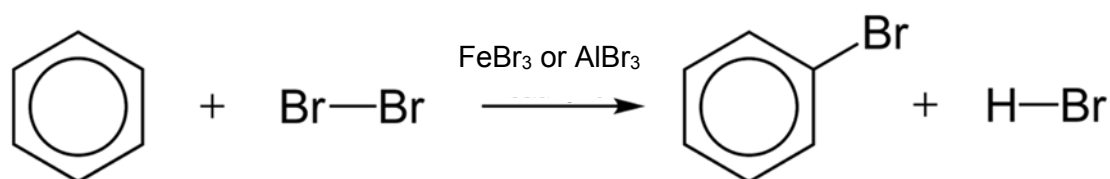
2 delocalised electrons  
 donated to electrophile,  
 forming a covalent bond.

C-H bond breaks and 2  
 electrons are returned to  
 the delocalised ring.

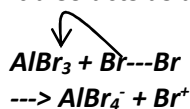
### 5. Halogenation of Benzene

**Benzene won't react with halogens on their own, so a halogen carrier catalyst is used to generate a halogen ion.**

**This catalyst is changed depending on the halogen, so for substitution of chlorine it is  $\text{FeCl}_3$  or  $\text{AlCl}_3$  etc.**



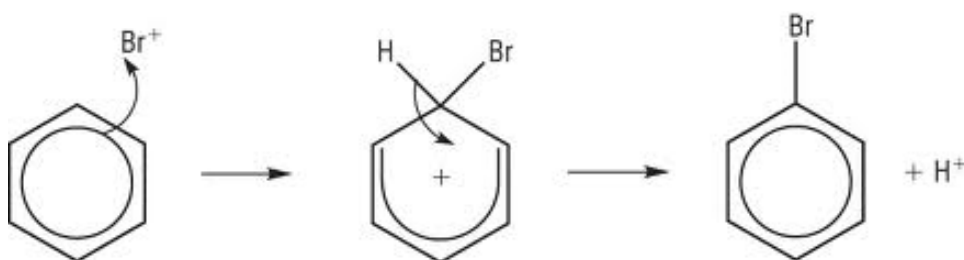
**The electron carrier polarises the Halogen, making it behave as an electrophile. It also acts as a catalyst.**



**The  $\text{H}^+$  ion from the benzene ring then reacts with the  $\text{AlBr}_4^-$  to regenerate  $\text{AlBr}_3$**

**This may be used in certain Pharmaceuticals, and Chlorobenzene can be used in Pesticides.**

**Halogenation –  $\text{X}_2 + \text{FeX}_3 \text{ ----> } \text{X}^+ + \text{FeX}_4^-$  (where X is a halogen)**



**Benzene is too stable to react with Halogens so reacts with a halogen carrier.**

**You can also add Alkyl groups by reaction a Haloalkane with AlX<sub>3</sub>  
This generates the Alkyl ion (CH<sub>3</sub><sup>+</sup>) which can be added to Benzene,  
Whilst the same happens to the catalyst before.**

#### 6. Stability and Electron density of Benzene and Alkenes

**When Bromine is added to an alkene it changes from orange to colourless**

**Br<sub>2</sub> is a non polar molecule, but still reacts with double bonds in alkenes**

- **The  $\pi$  bond contains localised electrons above and below the plane of the carbon atoms in a double bond, which produces a region of high electron density.**
- **When Bromine approaches an alkene, the electrons in  $\pi$  bond repel the Br-Br bond – this induces a dipole in the Br<sub>2</sub> molecule, making it polar.**
- **The  $\pi$  electron pair is attracted to the  $\delta^+$  Br atom, causing the C=C bond to break.**
- **The  $\delta^+$  Br atom forms a bond between itself and one of the carbon atoms, breaking the Br-Br bond by heterolytic fission, leaving a Br<sup>-</sup> ion. This creates a carbocation due to a positively charged Carbon.**
- **The Br<sup>-</sup> ion is attracted to the Carbocation, forming a covalent bond and the end product.**

**This reaction occurs since the electrons in the  $\pi$  bond are localised between the 2 carbon atoms, so can induce Bromine.**

**When bromine is added to Benzene, no reaction takes place – if FeBr<sub>3</sub> is added, however, the reaction does occur.**

**Benzene is unable to react without a halogen carrier –**

- **It has delocalised  $\pi$  electrons spread over all 6 carbon atoms, whereas alkenes have localised electrons above and below the 2 carbon atoms in a C=C bond.**
- **Benzene has a lower  $\pi$  electron density than alkenes**
- **There is insufficient  $\pi$  electron density to polarise a Br-Br bond in Benzene – so it is resistant to reactions with non-polar halogens**
- **A halogen carrier generates a more powerful electrophile Br<sup>+</sup> which can attract the  $\pi$  electrons from Benzene so the reaction can occur.**

#### 7. Phenol

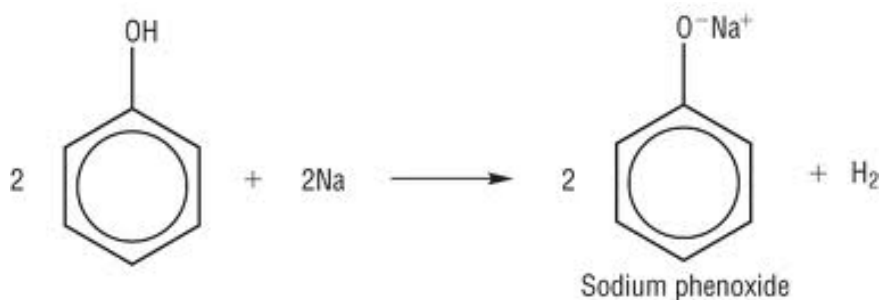
**Phenols are a class of organic compounds with an –OH group attached to a Benzene ring.  
If the –OH group is attached to a side chain, however, an aromatic alcohol is produced.  
Phenols are soluble in water due to the -OH group, but less soluble than alcohols due to the presence of the Benzene ring.**

**Acidity of compounds depends on electronegativity of added group. (FOCINBrKr)  
E.g In Phenol, which has an OH group. The O is more electronegative than the N, the electrons are drawn into the Benzene ring, increasing its reactivity. So it is electron releasing, rather than withdrawing.**

## 8. Reactions with Phenol

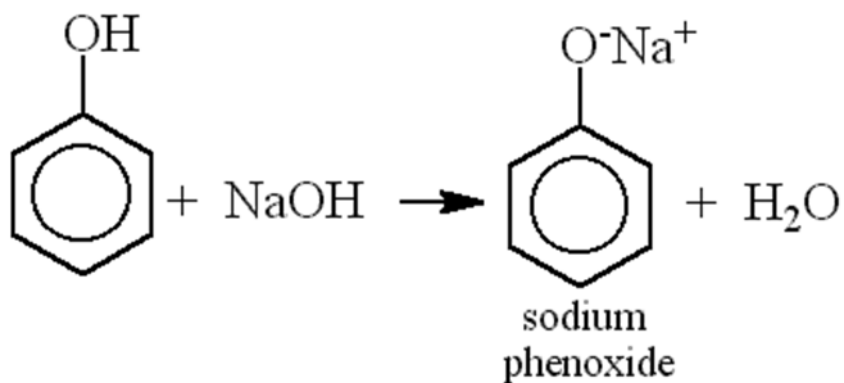
With Sodium:

**Phenol + Sodium -----> Sodium Phenoxide + Hydrogen**



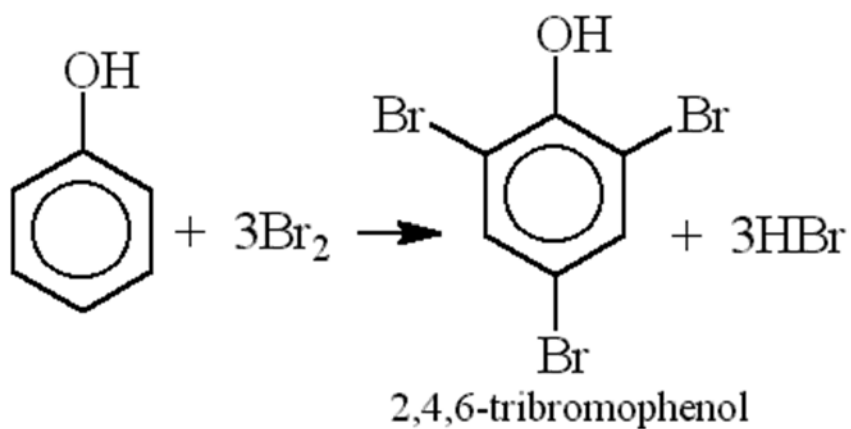
With Sodium Hydroxide

**Phenol + Sodium -----> Sodium Phenoxide + Water**



(ii) with bromine to form 2,4,6-tribromophenol;

**Phenol + Bromine Water -----> 2,4,6-tribromophenol + Hydrogen Bromide**



## 9. Stability and reactivity of Phenol

**Phenol can be brominated more easily than Benzene**

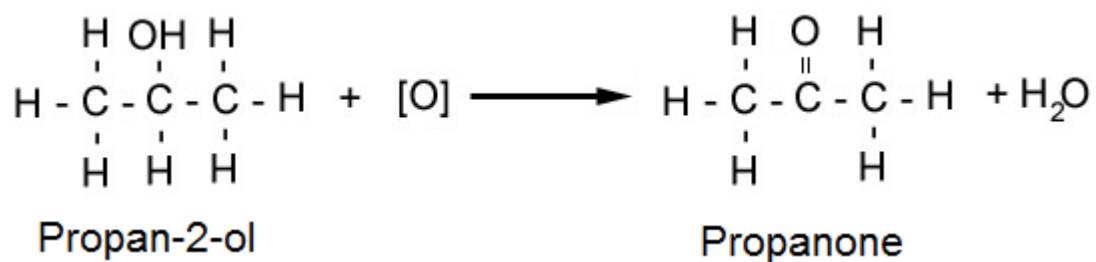
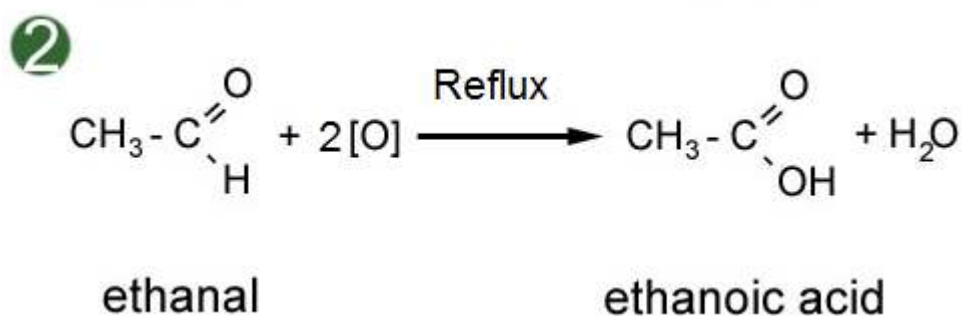
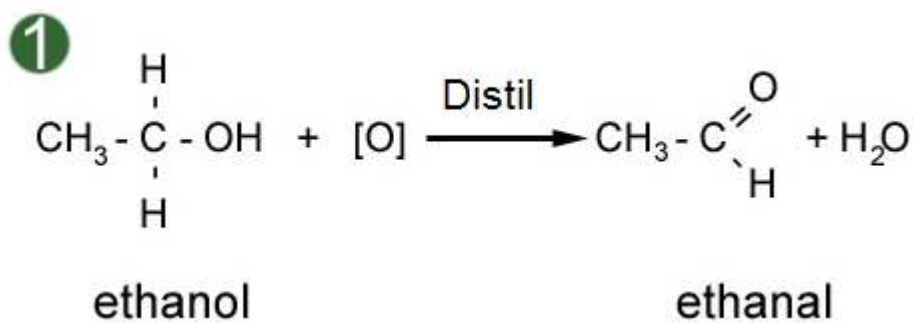
- A lone pair of electrons on the oxygen atom is drawn into the Benzene ring.
- This increases the electron density
- This increased electron density allows Bromine to be polarised.
- More vigorous reactions will occur in Phenol due to this.

## 10. Uses of Phenols

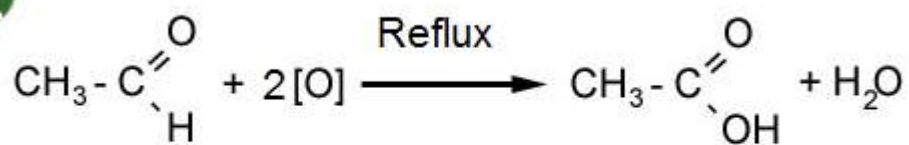
**Phenols can be used as:**

Phenol	Use
Alkyl Phenols	Surfactants and Detergents
Chlorophenols	Antiseptics and Disinfectants
Salicylic Acid	Aspirin
Bisphenol	Epoxy resins for paints

## 11. Oxidation of Carbonyl Compounds

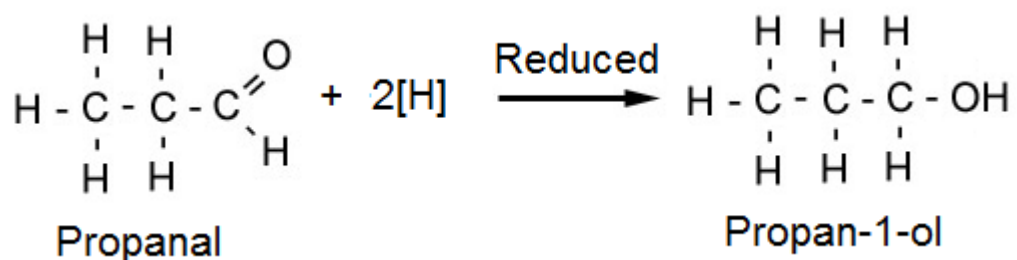
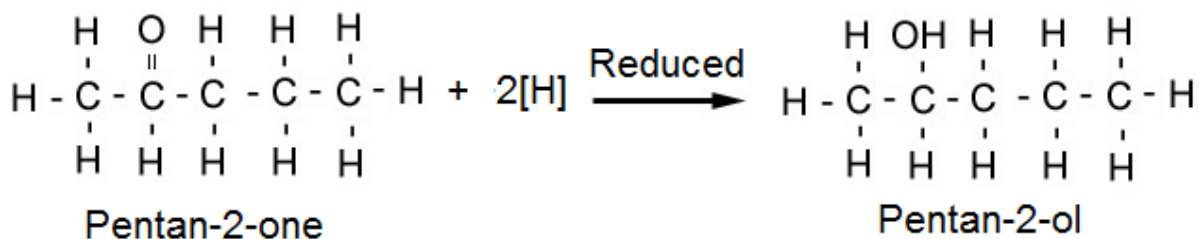
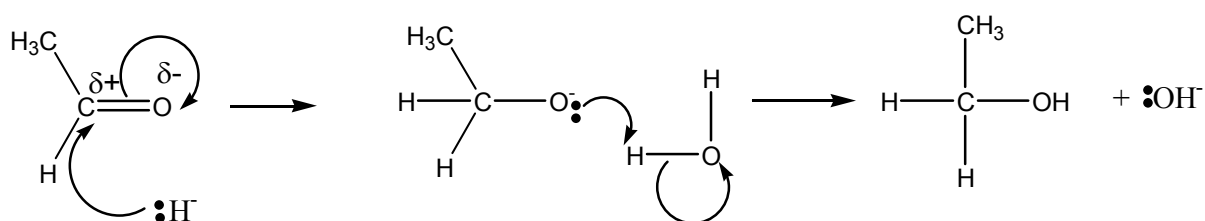


2



ethanal

ethanoic acid

12. Reduction of Carbonyl compoundsReduction of PropanalReduction of Pentan-2-one13. Nucleophilic substitution

#### 14. Testing for Carbonyl compounds

- **2,4-dinitrophenylhydrazine (2,4 – DNP) may be mixed with Methanol and Sulphuric Acid to form Brady's reagent.**
- **When this is added to an Aldehyde or Ketone, a yellow, orange precipitate is formed.**
- **This precipitate (2,4-dinitrophenylhydrazone derivative), confirms the presence of the functional group C=O**
- **This test cannot be used for Carboxylic Acids or Esters.**

The use of Tollens' reagent (ammoniacal silver nitrate) to:

- **After the previous test, Tollens' reagent (a weak oxidising agent) can be used to detect a Ketone or Aldehyde.**
- **Aldehydes are oxidised to form Carboxylic acids with Tollens'; Ketones are not.**

Tollens' Reagent can be formed by:

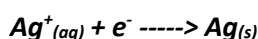
- **Adding Aqueous Sodium Hydroxide to Aqueous Silver Nitrate until a brown precipitate of Silver oxide is formed.**
- **Dilute Aqueous Ammonia is then added until the precipitate dissolves, forming a colourless solution.**

Detect the presence of an aldehyde group,

- **Aldehyde – Silver, grey solid (silver mirror) is formed.**
- **Ketone – No reaction**

#### 15. Distinguishing between Aldehydes and Ketones

**Aldehydes become oxidised by Tollens' reagent. Tollens' reagent is a weak oxidising agent, Aldehydes can be further oxidised, whereas Ketones cannot. Hence why there is no reaction with Ketones.**



**It is possible to identify the carbonyl compound by carrying out further experiments.**

1. **The Yellow/ orange solid formed is impure**
2. **It is filtered and recrystallized to form purified sample of 2,4-dinitrophenylhydrazone**
3. **The melting point of the purified derivative is measured and recorded.**
4. **The melting point is then compared to a pre-collected database**

#### 16. Solubility of Carboxylic Acids

**Carboxylic acids have highly polar C=O and O-H bonds so may form hydrogen bonds with water molecules.**

**As the number of Carbon atoms increases, the solubility decreases.**



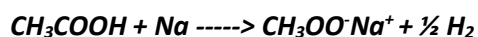
## 17. Reactions of Carboxylic Acids

**Carboxylic acids are weak compared to Nitric, Sulphuric and Hydrochloric Acid**

**They take part in several acid based reactions, such as forming Salts. These are known as Carboxylates.**

### With Metals:

**Carboxylic Acid + (Reactive) Metal ----> Salt + H<sub>2</sub>**

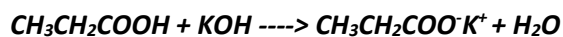


*Ethanoic Acid + Sodium ----> Sodium Ethanoate + Hydrogen*

*Remember to look at charge, if Mg was the metal, it has a 2+ charge, so CH<sub>3</sub>COOH would need to be doubled.*

### With Bases

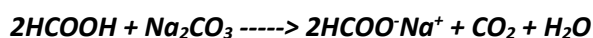
**Carboxylic Acid + Base ----> Salt + H<sub>2</sub>O**



*Propanoic Acid + Potassium Hydroxide ----> Potassium Propanoate + Water*

### With Carbonates

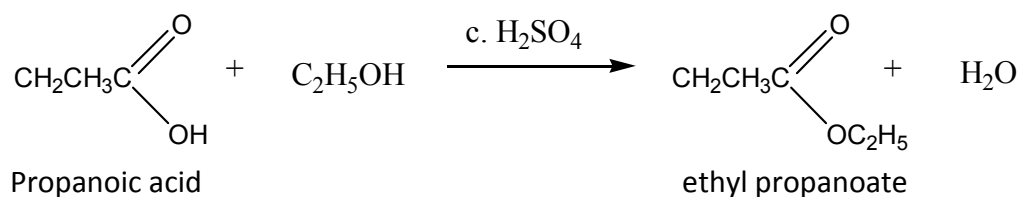
**Carboxylic Acid + Carbonate ----> Salt + H<sub>2</sub>O + CO<sub>2</sub>**



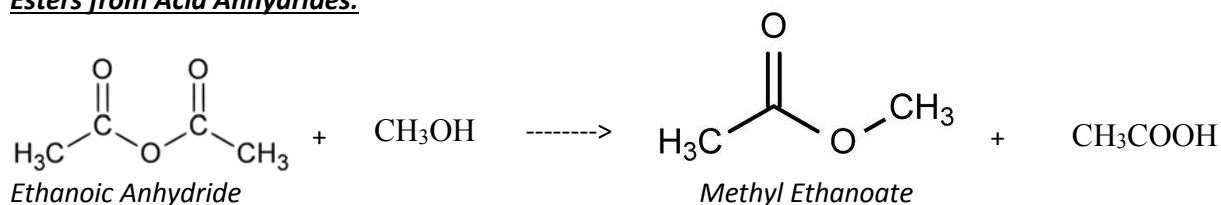
*Methanoic Acid + Sodium Carbonate ----> Sodium Methanoate + Carbon Dioxide + Water*

## 18. Esterification

### Esters from Carboxylic Acids:

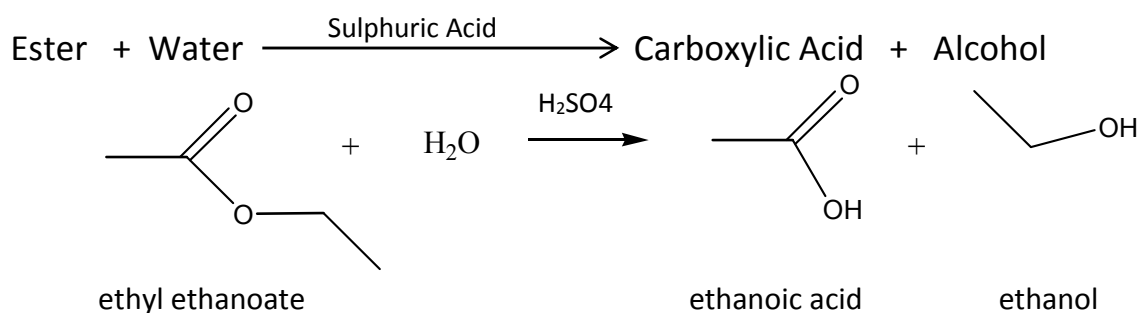


### Esters from Acid Anhydrides:

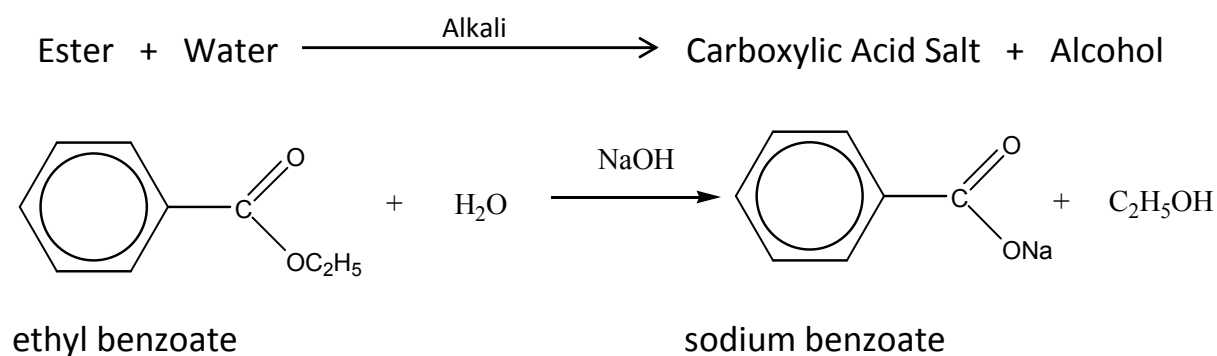


### 19. Hydrolysis of Esters

(i) in hot aqueous acid to form carboxylic acids and alcohols,



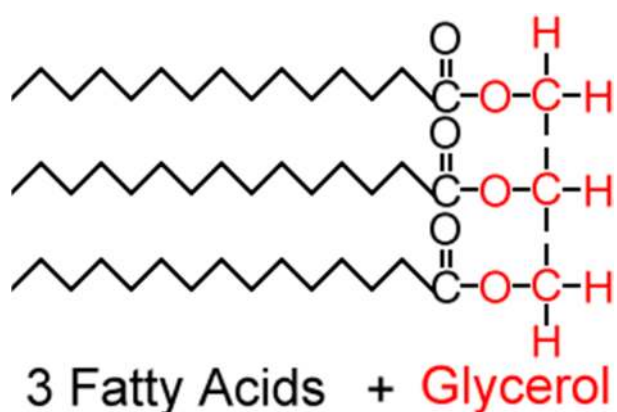
(ii) in hot aqueous alkali to form carboxylate salts and alcohols;



(e) state the uses of esters **in perfumes and flavourings**;

### 20. Triglycerides

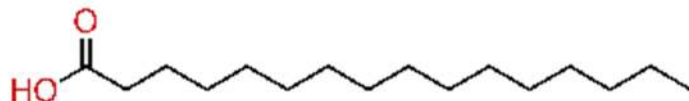
(f) describe a triglyceride as a **tri-ester of glycerol (propane-1,2,3-triol) and fatty acids**;



## 21. Types of fats and naming them

<i>Saturated Fatty Acid/ Fat</i>	<i>No C=C bonds</i>
<i>Monounsaturated Fats</i>	<i>1 C=C bond</i>
<i>Polyunsaturated Fats</i>	<i>More than 1 C=C bond</i>

### Naming Fatty Acids



**First number is no of carbon atoms**

**Second number indicates number of carbon-carbon double bonds**

**Third number in brackets is position of double bonds.**

**So Hexadecanoic acid is 16:0(0) or 16:0**

### Cis/Trans isomers of Fatty Acids

- **Restricted rotation about the double bond**
- **Unsaturated Fats come as Cis or Trans**
- **Trans fats present danger to us**
- **In the Cis form, the fatty acids do not pack closely together so exist as liquid at room temperature.**
- **In the trans form, the chain is linear and the fatty acids pack closely together, giving it a high melting point, making it hard to remove from our system.**

## 22. Fats in the diet

**Lipoproteins are particles that carry lipids, such as cholesterol and fat, through the blood.**

**HDL's are formed from cholesterol, unsaturated fat and protein, they move cholesterol from the body tissue to the liver where they are converted to bile – these are 'good lipoproteins'.**

**LDL's are formed from cholesterol, saturated fat and protein, they move cholesterol from the liver to the body tissue where it may be deposited under the endothelium – these are 'bad lipoproteins'**

**Trans-fats raise LDL level and act as saturated fats – this increases the chances of narrowing arteries leading to diseases such as Heart Disease and Stroke.**

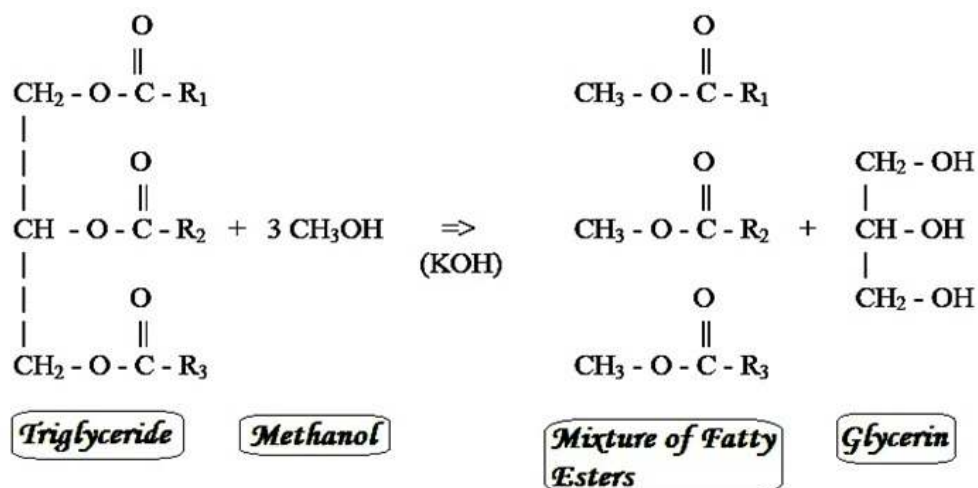
### 23. Using esters as Biodiesel

Esters may be used as a source of fuel due to high prices and lack of availability of Fossil Fuels.

The chemical structure of a biodiesel is an ethyl or methyl ester of a fatty acid.

Biodiesel is made by transesterification

Triglycerides are reacted with ethanol or methanol in the presence of sodium (or potassium) hydroxide catalyst



### 24. Amines

Amines are all derivatives of Ammonia so are weak bases.

They are proton acceptors as they

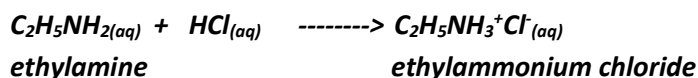
- Have a lone pair of electrons on the nitrogen atom
- Can accept a proton

When a base accepts a proton, a dative covalent bond forms between the lone pair on the nitrogen atom and the proton.

### 25. Reaction of Amines

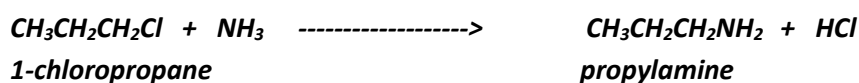
A primary amine is one in which the amine group is attached to a single carbon chain only.

**Primary Amine + Acid -----> Salt**

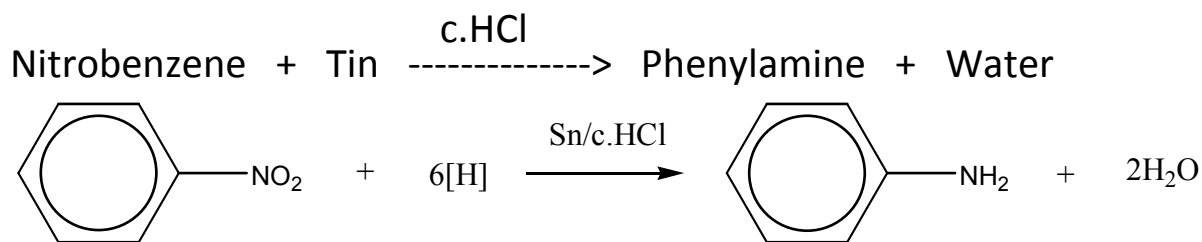


### 26. Preparing Amines

**Halogenoalkane + Ammonia -----> Amine + Hydrogen halide**



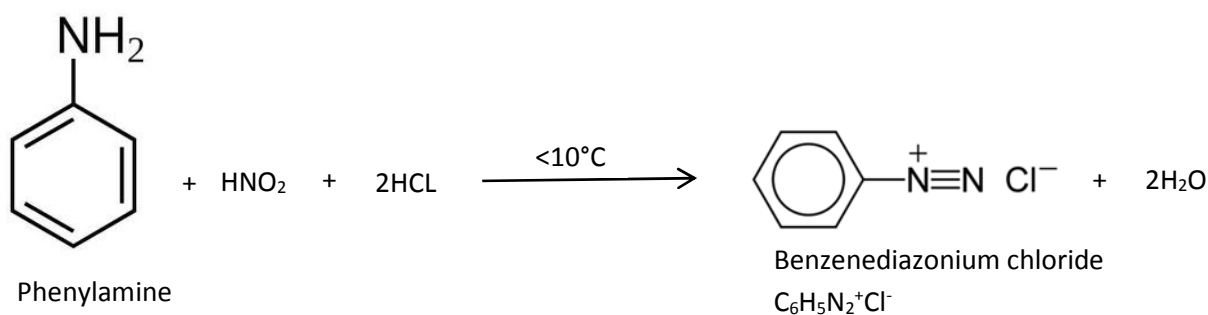
Ethanol is used as a Solvent and excess Ammonia is used – this stops further substitutions occurring



27. Synthesis of Azo-dyes

Diazotisation

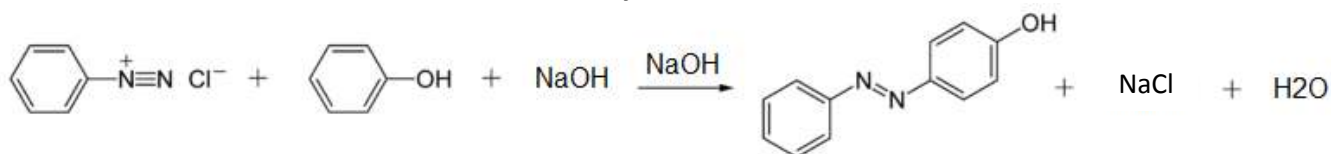
First, Nitrous Acid must be produced –  $\text{NaNO}_2 + \text{HCl} \rightarrow \text{HNO}_2 + \text{NaCl}$



Coupling

*Alkaline  
Conditions*

*Diazonium Salt + Phenol*  $\rightarrow$  *Azo Dye*



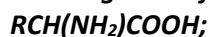
(e) state the use of reactions, such as (d), in the formation of dyestuffs.

# Module 2 – Polymers and Synthesis

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## 28. Amino Acids

Have a general formula of:



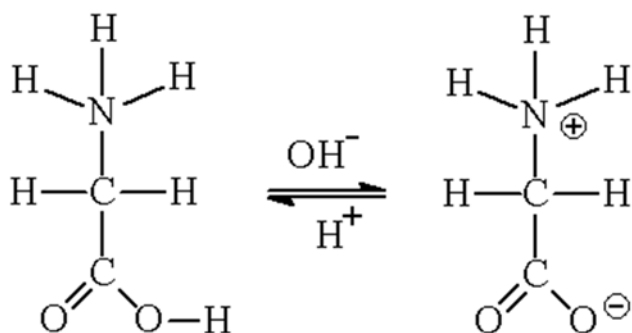
(b) state that **an amino acid exists as a zwitterion at a pH value called the isoelectric point;**

## 29. Zwitterions

**A zwitterion is an ion carrying both a positive and negative charge**

**An Acidic Carboxyl group and a basic amine group can interact together to form an internal salt, known as a zwitterion**

**E.g – Glycine**



*ion at low pH*

*zwitterion  
neutral pH*

## 30. Isoelectric points

**Isoelectric point is the pH in which there is no net electrical charge (where the Amino Acid exists as a zwitterion)**

(c) state that **different R groups in  $\alpha$ -amino acids may result in different isoelectric points;**

**Due to the differences in R groups, each amino acid has its own unique isoelectric point. Many have an isoelectric point close to pH 6 but some are much lower or higher.**

## 31. Properties of Amino Acids

**Amino Acids are amphoteric – they react with acids and bases**

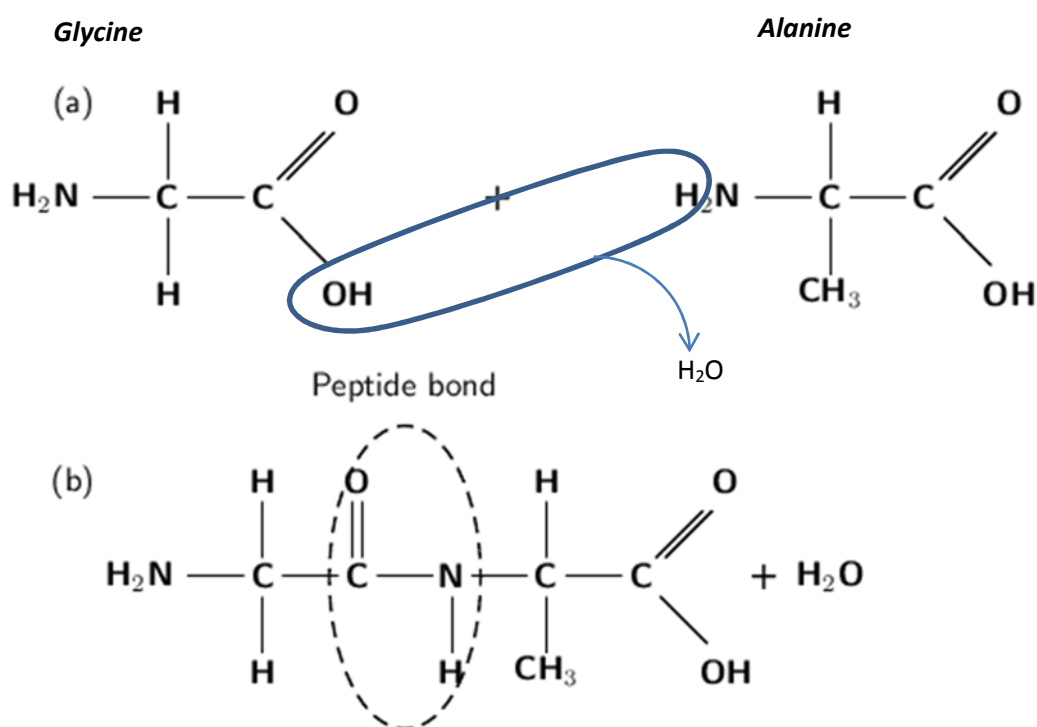
1. **When the pH is more acidic than the isoelectric point**
  - a. **The amino acid behaves as a base and accepts a proton from the acid**

- b. The Amino Acid forms a positively charged ion
- 2. At a pH more alkaline than the isoelectric point
  - a. The Amino acid behaves as an acid and donates a proton
  - b. The Amino Acid forms a negatively charged ion

32. Formation of polypeptides

Polypeptides are formed due to a condensation reaction. The elimination of a smaller molecule such as water occurs.

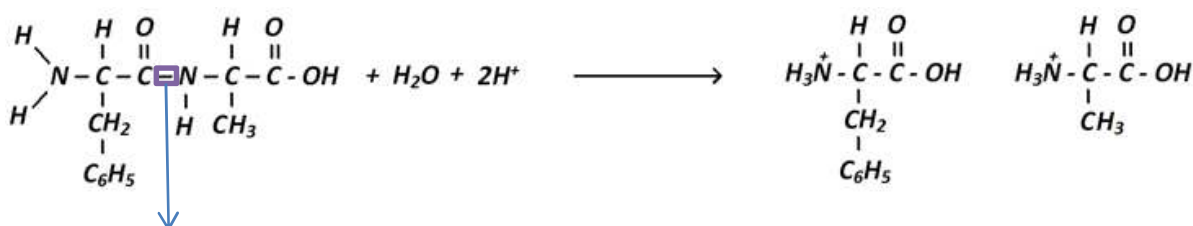
e.g Condensation of Glycine and Alanine



It is possible to form a different dipeptide if the Carboxylic Acid of Alanine reacts with the Amine group of Glycine instead.

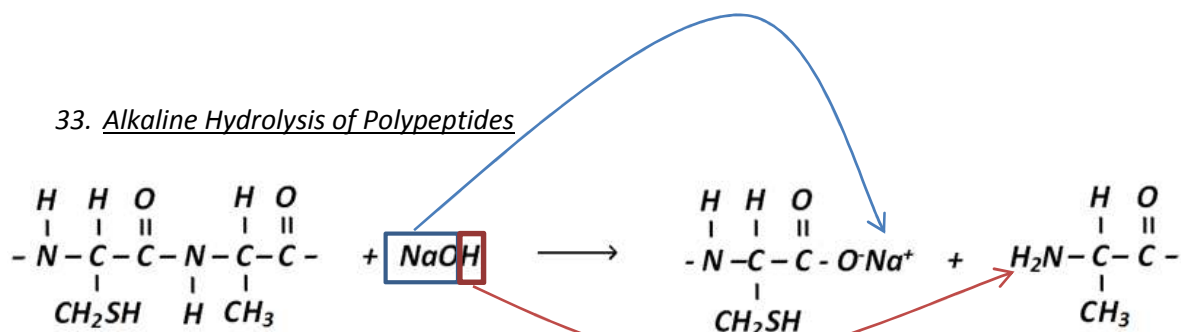
32. Acid Hydrolysis of Polypeptides

Positive ions formed



In hydrolysis, the bond is broken at where the former Carboxylic acid and former amine groups meet

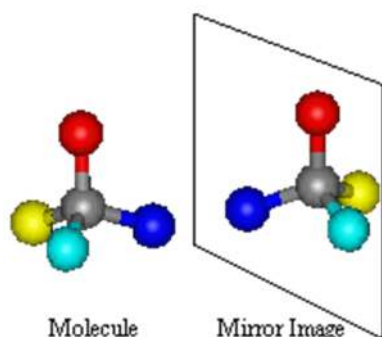
### 33. Alkaline Hydrolysis of Polypeptides



Polypeptide is broken down into amino acids in form of their sodium salts.

### 34. Optical Isomers

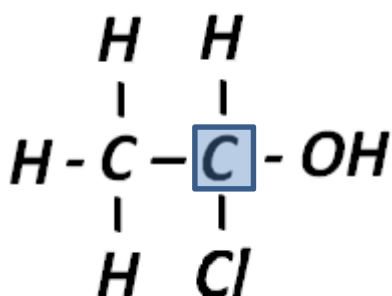
(g) describe optical isomers as **non-superimposable mirror images about an organic chiral centre**: four different groups attached to a carbon atom;



E.g -

(h) identify chiral centres in a molecule of given structural formula;

A chiral centre is a carbon atom which is attached to 4 different groups.



This Carbon atom is Chiral as it has 4 different groups attached.

(i) explain that optical isomerism and E/Z isomerism (see also unit F322: 2.1.1.f) are different types of stereoisomerism.

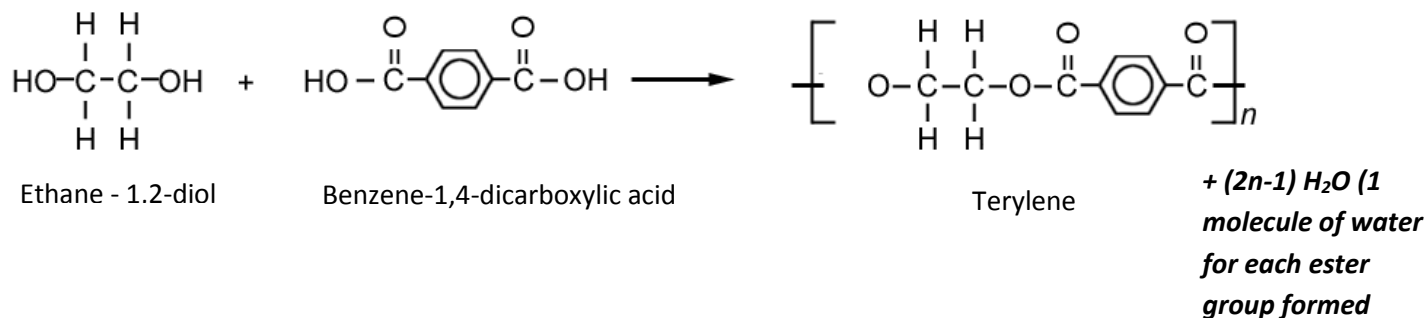
Both Optical isomerism and E/Z isomerism are forms of Stereoisomerism; they have the same structural formula but a different arrangement of atoms in space.



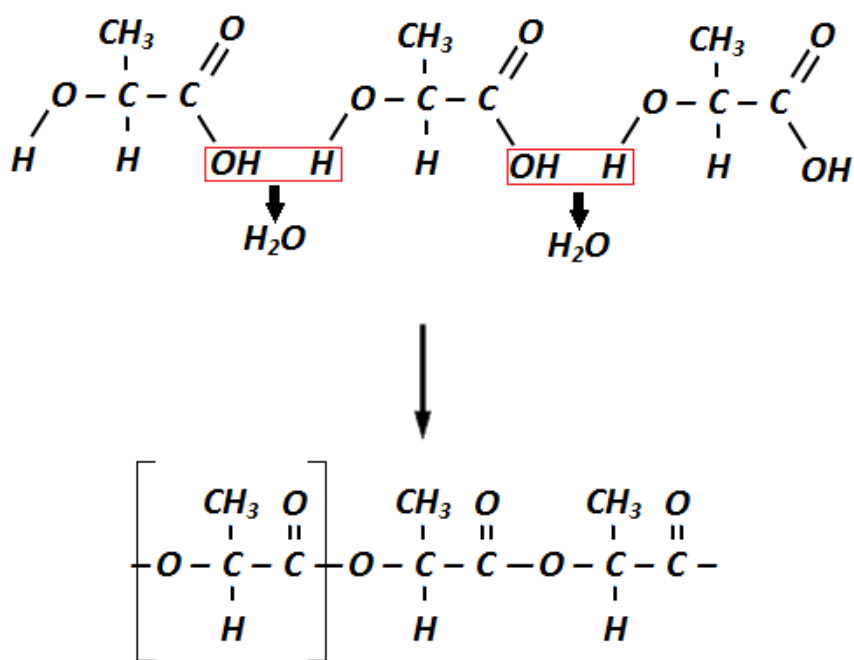
### 35. Formation of Polyesters

(i) polyesters, eg Terylene from benzene-1,4-dicarboxylic acid and ethane-1,2-diol, poly(lactic acid) from 2-hydroxypropanoic acid (lactic acid) (see (h) below),

#### Formation of Terylene



#### Formation of Poly(lactic acid)

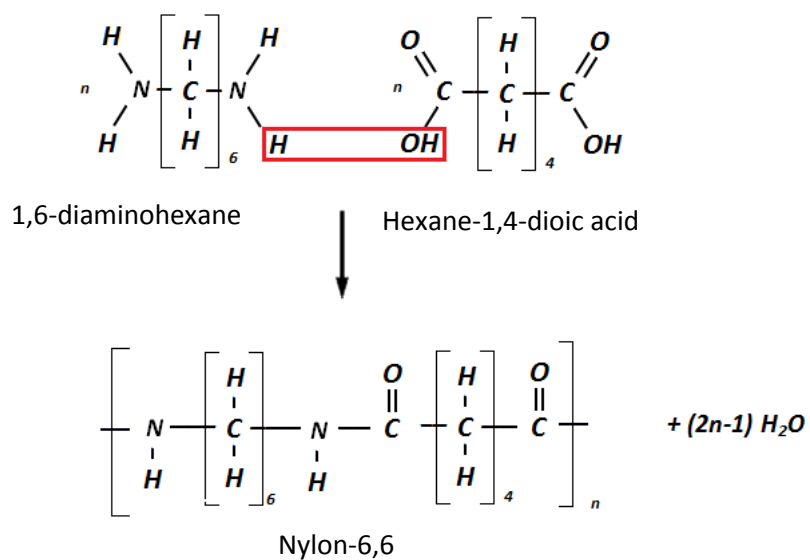


### 36. Formation of Polyamides

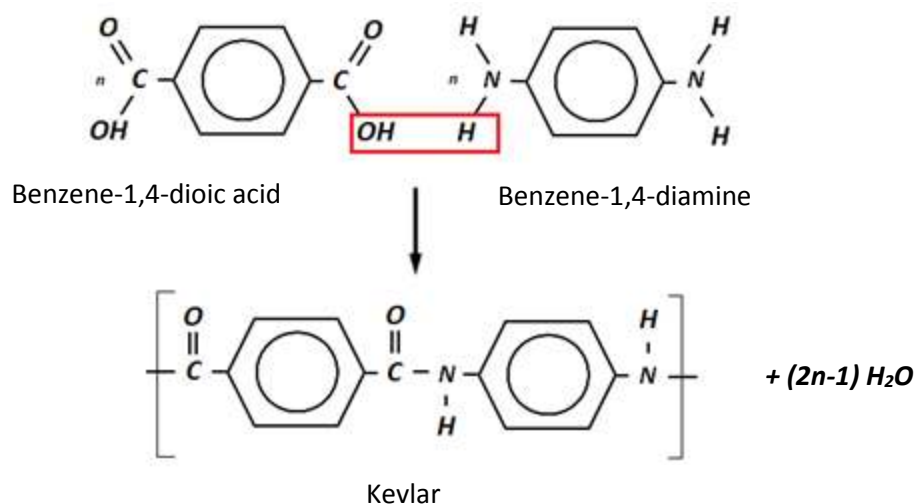
(ii) polyamides, eg nylon-6,6 from 1,6-diaminohexane and hexane-1,6-dicarboxylic acid,

Kevlar from benzene-1,4-diamine and benzene-1,4-dicarboxylic acid;

#### Formation of Nylon - 6,6



#### Formation of Kevlar



### 37. Types of Polymerisation

(b) compare condensation polymerisation with addition polymerisation (see also unit F322: 2.1.3.g-i);

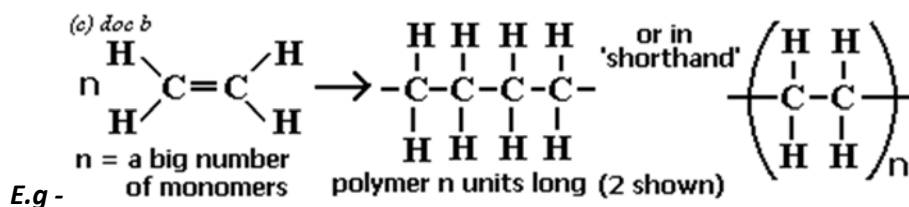
Feature	Addition Polymer	Condensation Polymer	
		Polyester	Polyamide
Functional Groups	C=C	-COOH and -OH	-COOH and -NH <sub>2</sub>
Type(s) of monomer	1	1 or 2	1 or 2
Product(s)	Poly(alkene)	Polyester + water	Polyamide + water

### 38. Suggesting type of Polymerisation

- C=C bond = Addition polymerisation
- 2 x monomer each with 2 x Functional group = condensation
- 1 x monomer; 2 x functional group = condensation
- Ester/Amide linkages = condensation
- Backbone is continuous chain of Carbon atoms = addition reaction and the monomer is an alkene.

(d) identify the monomer(s) required to form a given section of a polymer (and vice versa);

**The monomer is the unit that is repeated within the polymer. The double bond will form between the Carbons of the displayed formula shown in the repeat unit.**

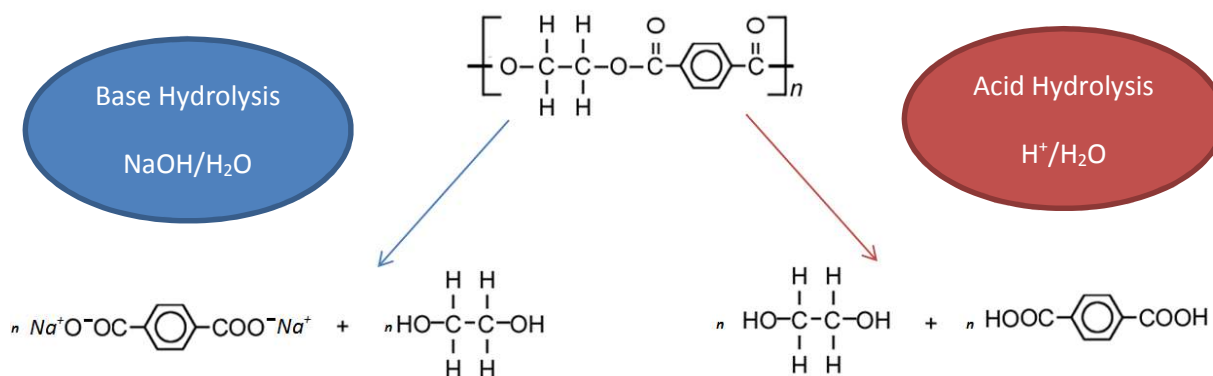


(e) state the **use of polyesters and polyamides as fibres in clothing**;

### 39. Acid and Base Hydrolysis of Polyesters and Polyamides

#### Hydrolysis of Polyesters

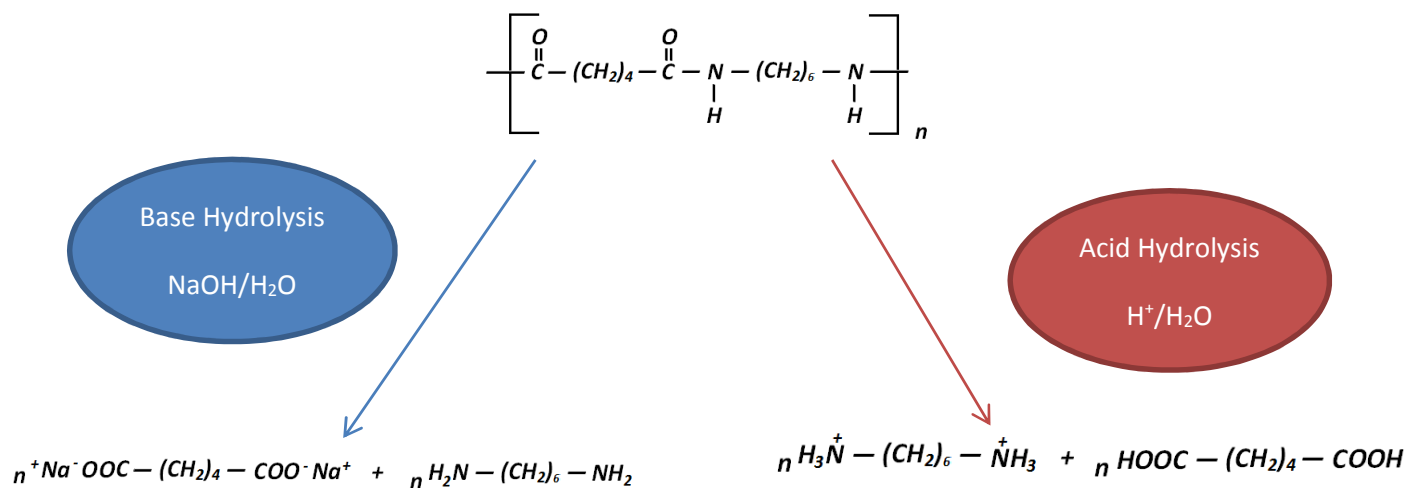
**Polyesters may also be hydrolysed by hot aqueous acid and aqueous alkali, although it is slower with Alkali's.**



**In basic conditions, the sodium salt of a carboxylic acid  $-\text{COO}^- \text{Na}^+$  is formed and a hydroxyl group  $-\text{OH}$**

**In acidic conditions, the monomer unit of the polyester is produced.**

#### Hydrolysis of Polyamides



**In acid conditions, a dicarboxylic acid is produced as well as an ammonium salt of the diamine**

**In basic conditions, the sodium salt of the dicarboxylic acid and the diamine is formed.**

40. Minimising Waste through use of Biodegradable products.

**A lot of the products we use today may damage the environment. Due to environmental pressures and cost of crude oil, biodegradable products are being designed.**

**Some polyesters have been derived to replace oil-based products.**

- **Poly(lactic acid) is used in compost bags and disposable tableware**
- **Poly(glycolic acid) is used in surgery for stitches.**
- **Synthetic polyesters may be used as thermoformed trays for fresh produce and meat.**

*(h) explain that condensation polymers:*

*(i) may be photodegradable as the C=O bond absorbs radiation,*

*(ii) may be hydrolysed at the ester or amide group.*

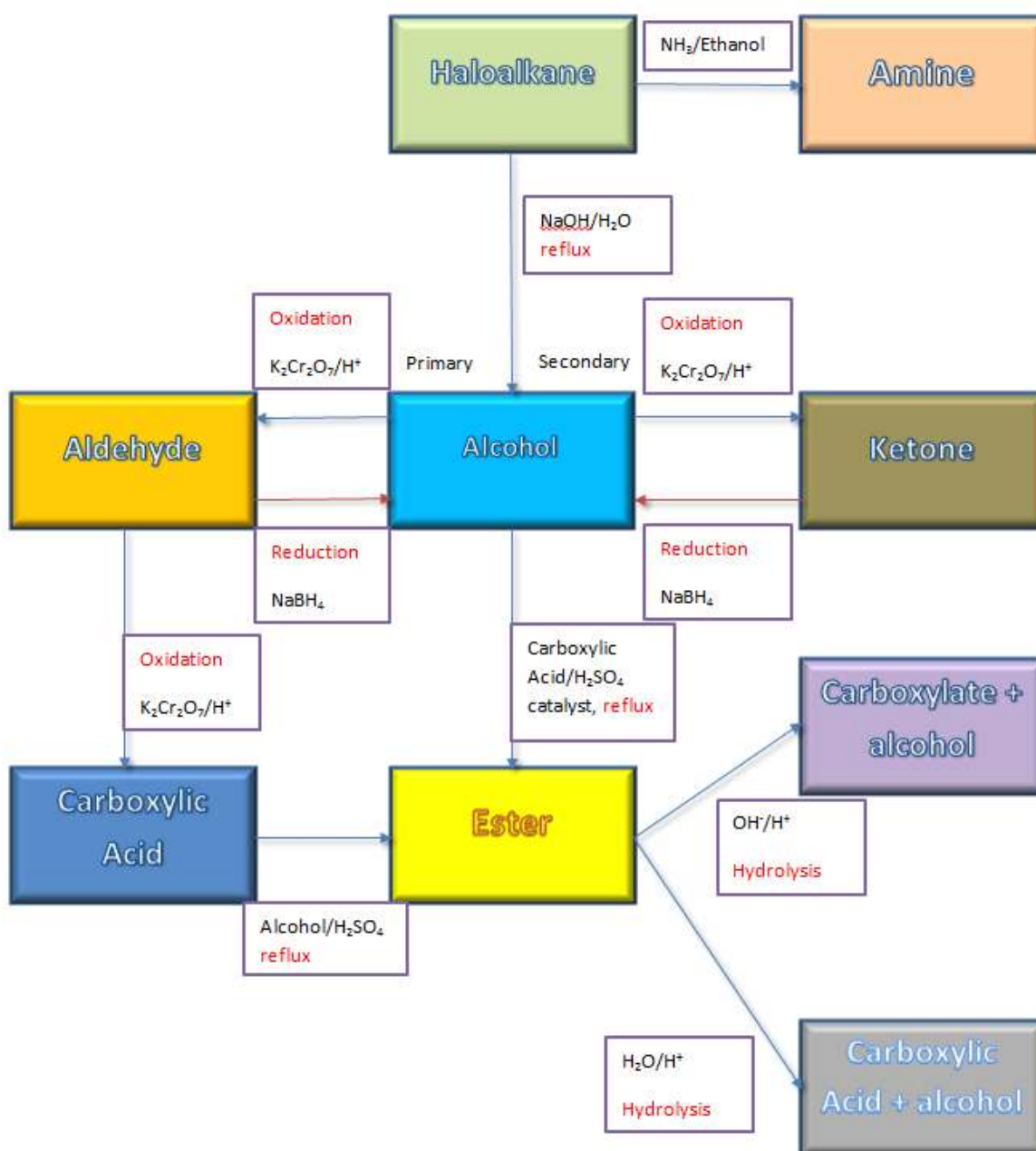
*(a) for an organic molecule containing several functional groups:*

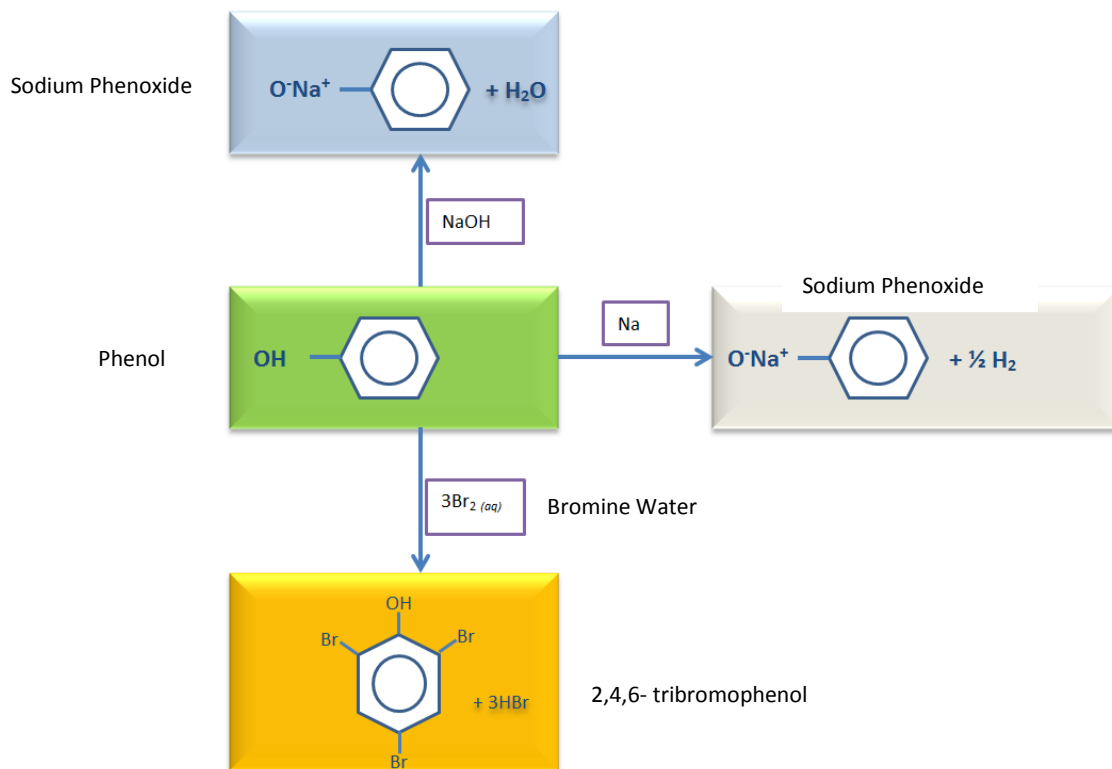
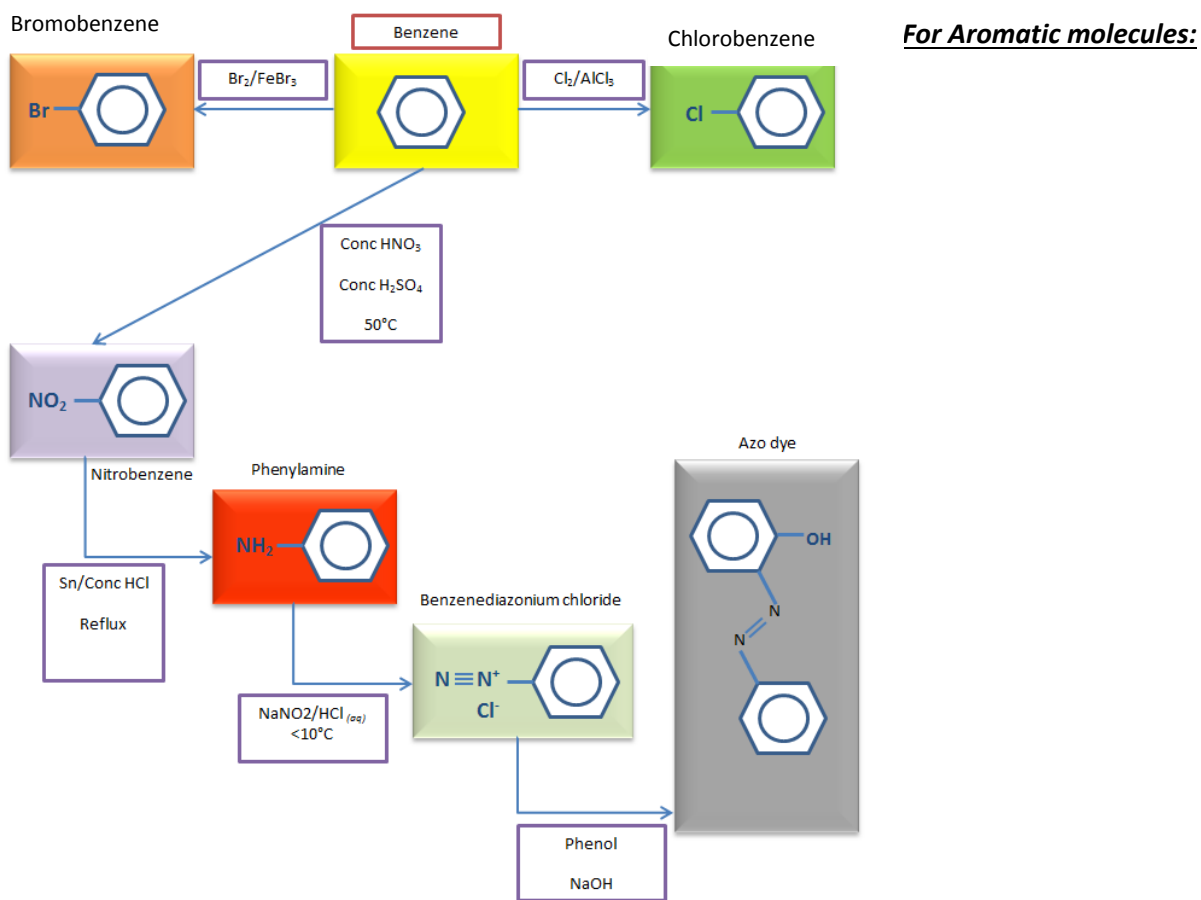
*(i) identify individual functional groups,*

*(ii) predict properties and reactions;*

**See Below**

For Aliphatic molecules





#### 41. Deducing synthetic routes of organic compounds

(b) devise multi-stage synthetic routes for preparing organic compounds;

1. **When given a question, check the carbon skeleton of the original reagent and the final product – longer products mean that two carbon chained compounds must be reacted together.**
2. **See if you can spot the change in the reaction, look out for different functional group, chain lengths etc.**
3. **Try to work backwards, using retro-synthesis.**

#### 42. Isomerism in Industry

(c) explain that **the synthesis of pharmaceuticals often requires the production of a single optical isomer;**

**A single optical isomer usually contains the desired therapeutic effect, however when a chiral compound is synthesised, a mixture of optical isomers may be produced which have very different, undesired effects or problems.**

(d) explain that **molecules prepared synthetically in the laboratory often contain a mixture of optical isomers, whereas molecules of the same compound produced naturally by enzymes in living systems will often be present as one optical isomer only;**

(e) explain that the synthesis of a pharmaceutical that is a single optical isomer:

- (i) **increases costs due to difficulty in separating the optical isomers,**
- (ii) **reduces possible side effects and improves pharmacological activity;**

(f) explain that modern synthesis of a pharmaceutical with a single optical isomer is often carried out:

- (i) **using enzymes or bacteria which promote stereo-selectivity,**
- (ii) **using chemical chiral pool synthesis or chiral Catalysts.**

**This makes use of naturally occurring chiral molecules within a synthetic route – the chirality of the original molecule can lead to the formation of a product that is a single, pure isomer.**

**Chiral catalysts are formed through the use of transition element complexes. These can transfer their chirality to synthesis a single isomer product.**

- (iii) **using natural chiral molecules, such as Amino acids or sugars,**



# Module 3: Analysis

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## 43. Chromatography

(a) describe chromatography as **an analytical technique that separates components in a mixture between a mobile phase and a stationary phase;**

**E.g – separation of pigments in leaves.**

**The mobile phase may be a liquid or a gas,  
The mobile phase is the phase that moves in chromatography, it moves in a definite direction.**

**The stationary phase may be a solid on a solid support (as in thin-layer chromatography, TLC) or either a liquid or solid on a solid support (as in gas chromatography, GC);**

**The stationary phase does not move in chromatography**

(c) state that:

(i) **a solid stationary phase separates by adsorption, - (in Thin Layer Chromatography (TLC))**

**In adsorption, the component molecules bind to the solid stationary phase. The stronger the adsorption to the stationary phase, the more the component molecules are slowed down.**

(ii) **a liquid stationary phase separates by relative solubility;**

**Components dissolve in the liquid stationary phase. The greater the solubility, the more the component molecules are slowed down.**

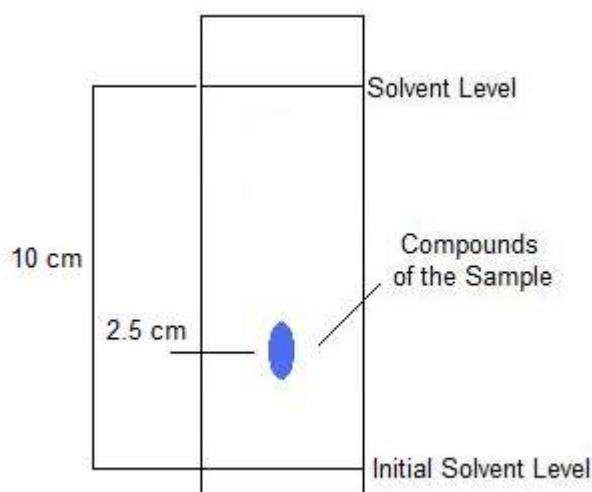
(d) explain the term  $R_f$  value, and interpret one-way chromatograms in terms of  $R_f$  values;

**An  $R_f$  value shows how far a component has moves compared with the solvent front.**

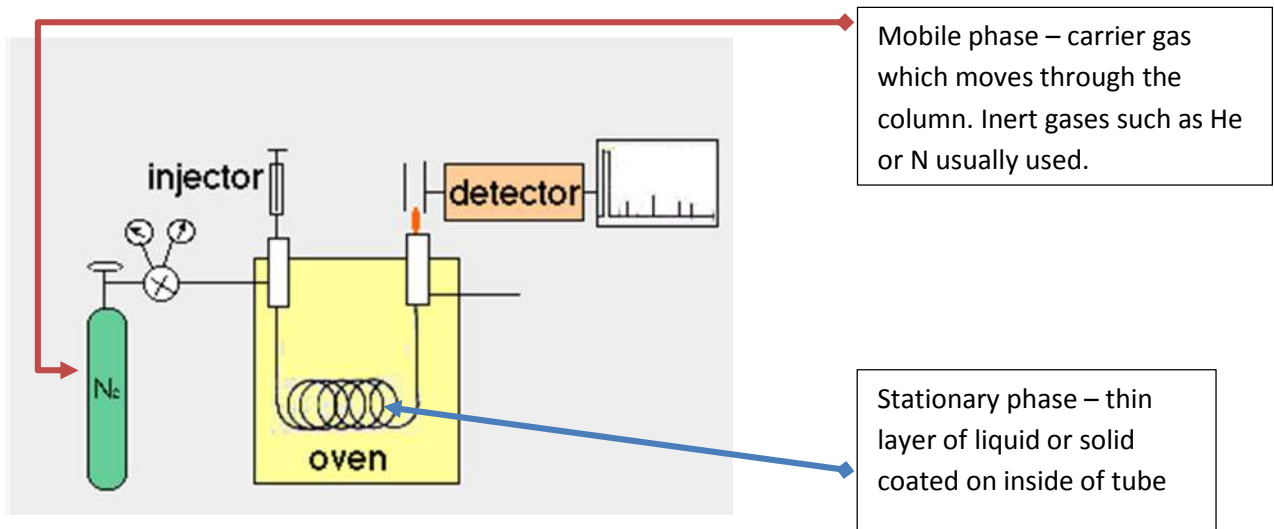
**In this diagram, the solvent has moves 10cm, and the sample has moves from the initial solvent level up 2.5 cm.**

**It therefore has an  $R_f$  value of  $2.5/10$   
 $=0.25$**

**This value can then be compared to one of the known, pure compounds for identification.**

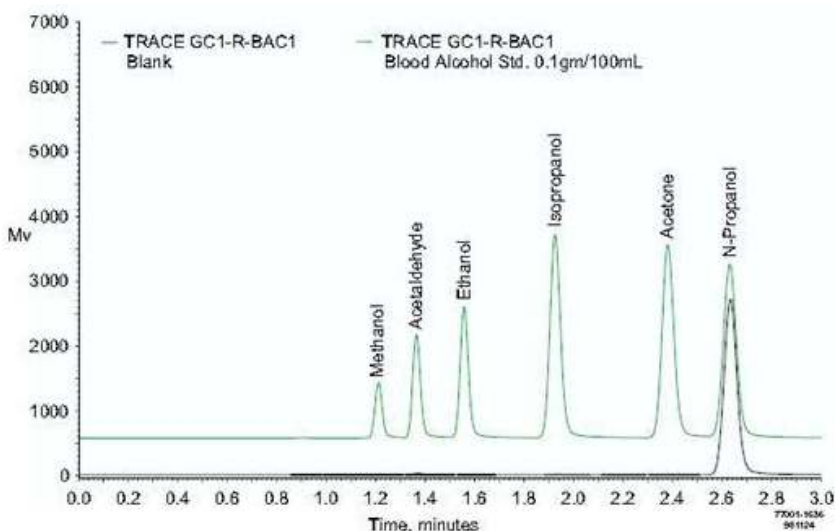


#### 44. Gas Chromatography



**Retention time - In gas chromatography, the time for a component to pass from the column inlet to the detector.**

1. **The mixture is injected into the chromatograph and vaporised.**
2. **The mobile carrier gas flushes the mixture through the column**
3. **Components of the mixture slow down whilst interacting with stationary phase.**
  - a. **If the lining is liquid, the components may dissolve**
  - b. **If the lining is solid, the components become adsorbed to the surface**
4. **The carrier gas flushes the components further along the tube.**
5. **Different compounds are slowed due to their solubility or adsorption rate, the greater the slower, this separates the components out.**
6. **Each component leaves the column at a different time and is detected, the results are displayed on a graph.**



**The graph shows the different retention times, which can be compared to known compounds to help identification.**

**The area under each peak is proportional to the amount of compound in a sample.**

45. Limitations of Gas Chromatography

**(i) similar compounds often have similar retention times,**

**(ii) Not all substances may be separated and detected.**

**(iii) unknown compounds have no references that can be compared to – so this only works for known substances.**

46. Using Mass Spec with Gas Chromatography

**(i) to provide a far more powerful analytical tool than from chromatography alone,**

**Mass spec can provide detailed structural information, however it cannot separate mixtures. GC can separate them first but cannot analyse them properly. Combining results can give a more conclusive answer as to what a certain compound may be.**

**(ii) to generate mass spectra which can be analysed or compared with a spectral database by computer for positive identification of a component;**

- 1. Separating and finding retention time can provide a initial identification**
- 2. Direct separated compounds into Mass spectrometer to be detected**
- 3. Analyse mass spectrum through comparison of spectral database.**
- 4. A mass spectrum is unique and definitive for a single compound, which allows a more positive identification.**

47. Uses of GC and MS in Industry

**Forensics: Analysis of small particles – can identify presence of particular substances for critical evidence.**

**Environmental analysis: Monitoring and analysing organic pollutants in the environment, including quality of waste water and drinking water and detecting pesticides in food.**

**Airport security: Detection of explosives in luggage and on human beings.**

**Space probes: Collect and analyse materials from other planets.**

48. NMR

**(a) state that NMR spectroscopy involves interaction of materials with the low-energy radiowave region of the electromagnetic spectrum;**

#### 49. Carbon 13 NMR

(b) analyse a carbon-13 NMR spectrum of a simple molecule to make predictions about:

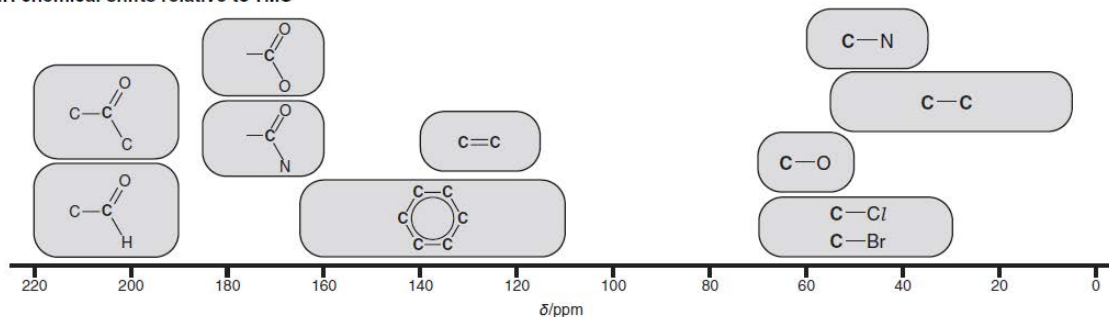
(i) the different types of carbon present, from chemical shift values,

**Chemical shifts in Carbon-13 NMR indicate the chemical environments of the carbon atoms present.**

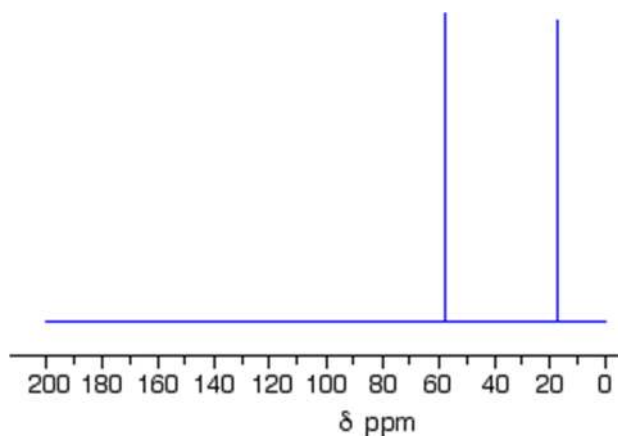
**The presence of an electronegative atom or group causes a significant chemical shift ( $\delta$ )**

(ii) possible structures for the molecule;

<sup>13</sup>C NMR chemical shifts relative to TMS



#### 50. C-13 NMR Spectra of Ethanol



carbon environment	chemical shift (ppm)
C=O (in ketones)	205 - 220
C=O (in aldehydes)	190 - 200
C=O (in acids and esters)	170 - 185
C in aromatic rings	125 - 150
C=C (in alkenes)	115 - 140
RCH <sub>2</sub> OH	50 - 65
RCH <sub>2</sub> Cl	40 - 45
RCH <sub>2</sub> NH <sub>2</sub>	37 - 45
R <sub>3</sub> CH	25 - 35
CH <sub>3</sub> CO-	20 - 30
R <sub>2</sub> CH <sub>2</sub>	16 - 25
RCH <sub>3</sub>	10 - 15

**There are 2 peaks shown above, this means that there are 2 carbons and they are in 2 carbon environments. A different environment means an atom is bonded to different atoms or groups of atoms**

**There are peaks at about 58 ppm and 18 ppm.**

**Using the shift spectrum above, the 18 ppm shows us the peak at 18 ppm is responsible for the C-C bond (the first environment)**

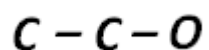
**Again, using the shift spectrum, the peak at 58 ppm signifies the C-O bond. (the second**

environment)

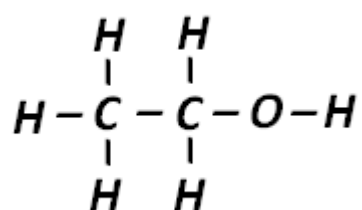
If Ethanol has a formula of  $C_2H_5OH$  we can predict the structure of the compound.

We know that there are two carbon environments which suggests there must be a C-C bond and a C-O bond

We are left with:

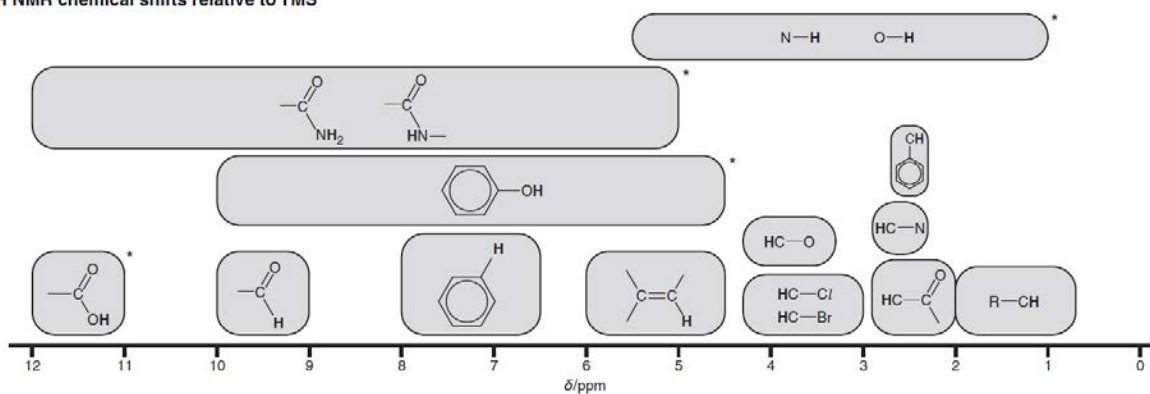


There are no structural isomers of ethanol however, due to there only being 2 carbon atoms. Therefore the formula must be:



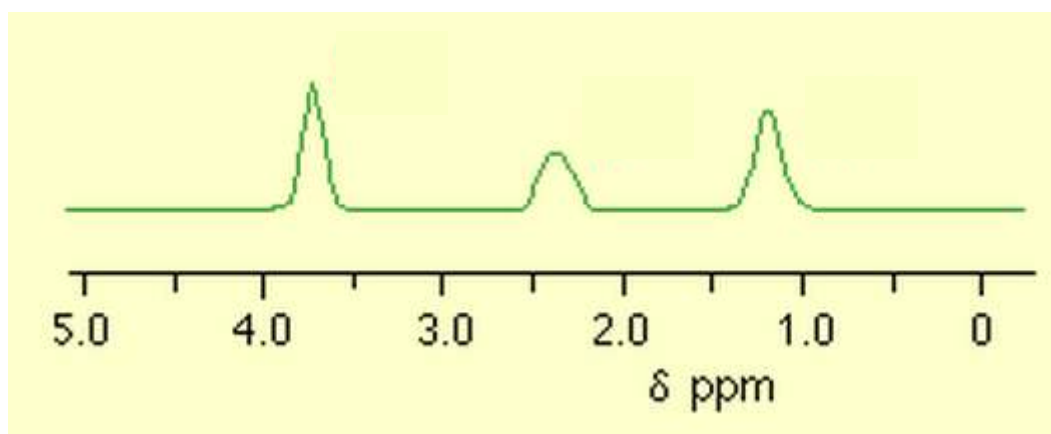
## 51. Proton NMR

<sup>1</sup>H NMR chemical shifts relative to TMS



**For  $\text{CH}_3\text{CH}_2\text{COOCH}_3$**

**There are 3 peaks so there are 3 proton environments**

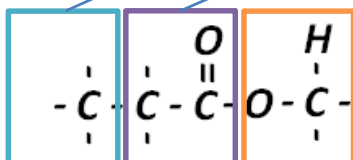


A peak at about 1.3 ppm suggests a  $\text{R-C[H]}$  group

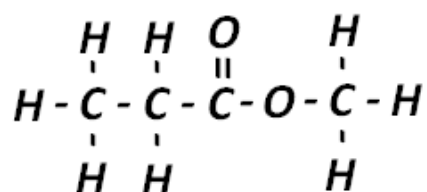
A peak at around 2.4 ppm suggests a  $\text{O=CC[H]}$  group

A peak at about 3.7 ppm suggests a  $\text{O-C[H]}$  group

With the given formula, we can work out from the suggested peaks that the shell of the formula is:



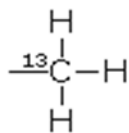
We can then piece the rest of the formula together to give:



## 52. Spin-Spin Coupling

The number of non-equivalent protons, or the protons on an adjacent carbon, can be determined using a spin-spin pattern and the  $n+1$  rule.

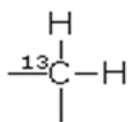
3 protons



$$n + 1 = 4$$



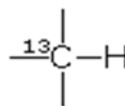
2 protons



$$n + 1 = 3$$



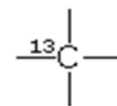
1 protons



$$n + 1 = 2$$



0 protons



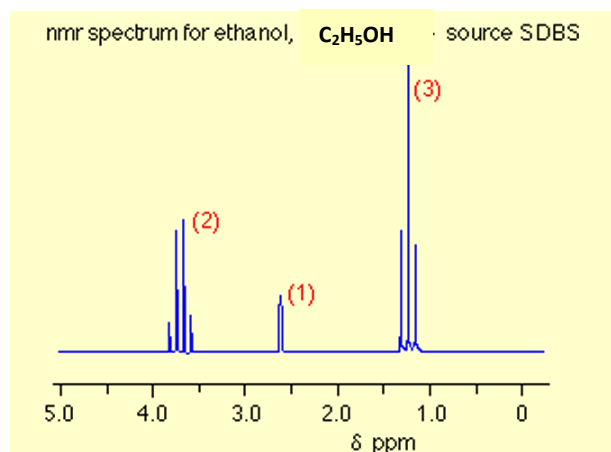
$$n + 1 = 1$$



For example. In the first peak, there are 4 sub peaks, using the  $n+1$  rule we can determine that there is a proton environment with a molecule containing 3 protons next to it. So there is basically an adjacent carbon on either side which has 3 protons attached.

However, this only allows you to determine the number of hydrogens on adjacent carbons, nothing more.

## 53. Deducing Structures of compounds from the use of NMR

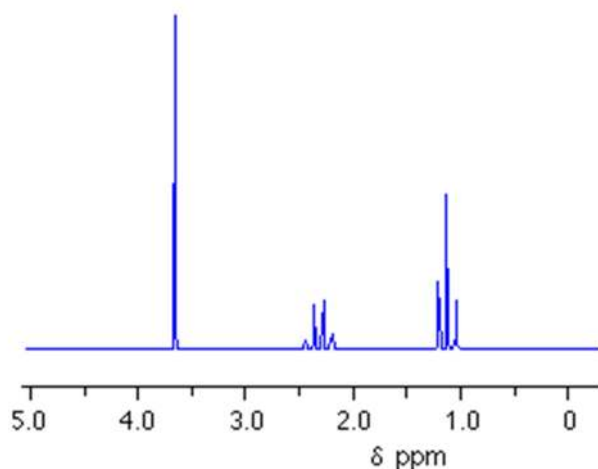


Referring to the Proton Chemical shift values,

1. We can see that the peaks at about 1.2-1.5 there is a triplet which suggests a  $\text{R-CH}_2$  value.
2. With the peak at about 2.6, there is a singlet, suggesting a  $\text{O-H}$  bond.
3. The peak at 3.5 – 3.9 is a quartet, suggesting a  $\text{O-C[H]}$  with 3 H's on an adjacent carbon
4. Putting this together, we can figure out the structure which is:
  - a. There are 2 carbons only.
  - b. The peak at 3.5 to 3.9, as well as the peak between 1.2-1.5 signifies that there there must be a  $\text{CH}_3\text{CH}_2$ , as a quartet and a triplet usually signify this.
  - c. Peak at 2.6 signifies an  $\text{O-H}$  bond, therefore  $\text{CH}_3\text{CH}_2\text{OH}$ , as there is nowhere else the  $\text{OH}$  can be added.

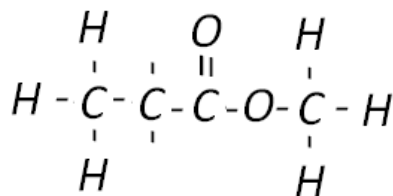
54. Using Chemical Shift and NMR to deduce structure.

high resolution nmr spectrum for methyl propanoate,  $C_4H_8O_2$

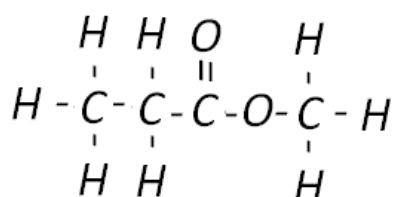


Using the chemical shift at each ppm:

1. There is a triplet at 1.0 ppm. This suggests a hydrogen with 2 adjacent protons, so a  $C_x-CH_2$ . We don't know how many hydrogens are on the first carbon, as the splitting pattern only tells us about the adjacent protons.
2. The quartet at 2.3 ppm suggests a carbon hydrogen with 3 adjacent protons, but also a  $C=O$ . So  $CH_3-CH_x-C=O$ . At this moment in time, we don't know how many hydrogens are on the middle carbon as we haven't pieced the evidence together yet.
3. A singlet at 3.7 ppm suggests hydrogen with no adjacent protons, and the carbon it's attached to, is also attached to an O. Therefore,  $O-CH_3$ . Bear in mind that the splitting tells us about adjacent protons. As there are no adjacent protons there must be 3 protons on the carbon.
4. So the evidence has told us that we have:
  - a.  $C_x-CH_2$
  - b.  $CH_3-CH_x-C=O$
  - c.  $O-CH_3$
5. As we have both the  $C=O$  from evidence b and the  $H_3C-O$  from c, we can tell that this will be an ester. So now we can piece the molecule together:
6. As we now know this is an ester, we can put together pieces b and c to get:



- a. Therefore, our  $CH_2$  from evidence a must go after our first  $CH_3$  to give us the overall structure found below





55. How chemical shift works

(e) describe the use of tetramethylsilane, TMS, as the standard for chemical shift measurements;

**Chemical shift is measured relative to a reference signal from the standard compound TMS (tetramethylsilane) –  $(\text{CH}_3)_4\text{Si}$**

**A molecule of TMS has 12 equivalent protons which give rise to a single sharp NMR signal which is = 0 ppm or  $\delta$**

**TMS is unreactive and volatile, so can be removed from the sample after running the NMR spectrum.**

(f) state the need for deuterated solvents, eg  $\text{CDCl}_3$ , when running an NMR spectrum;

**Deuterium is an isotope of hydrogen with one proton and one neutron, it has an even number of nucleons so produces no NMR spectrum.**

**Solvents such as  $\text{CDCl}_3$  are used. The carbon peak from  $\text{CDCl}_3$  can be removed from a Carbon-13 spectrum. The sample can also be recovered by evaporating off the  $\text{CDCl}_3$  solvent.**

(g) describe the identification of O–H and N–H protons by proton exchange using  $\text{D}_2\text{O}$ ;

**$\text{D}_2\text{O}$  can be used to filter out absorptions due to –OH and –NH protons.**

**$\text{D}_2\text{O}$  exchanged with the H present on –OH and –NH**

**$\text{D}_2\text{O}$  does not produce a NMR signal, which makes it easier to distinguish other absorption peaks.**

56. Uses of NMR

1. **A patient is placed in a cylindrical electromagnet**
2. **Radiowaves are sent through the body.**
3. **Protons align with, or against the magnetic field.**
4. **Protons resonate in response to pulses of radio – frequency radiation.**

**Advantages:**

- **Harmless**
- **Non – invasive**

**Disadvantages:**

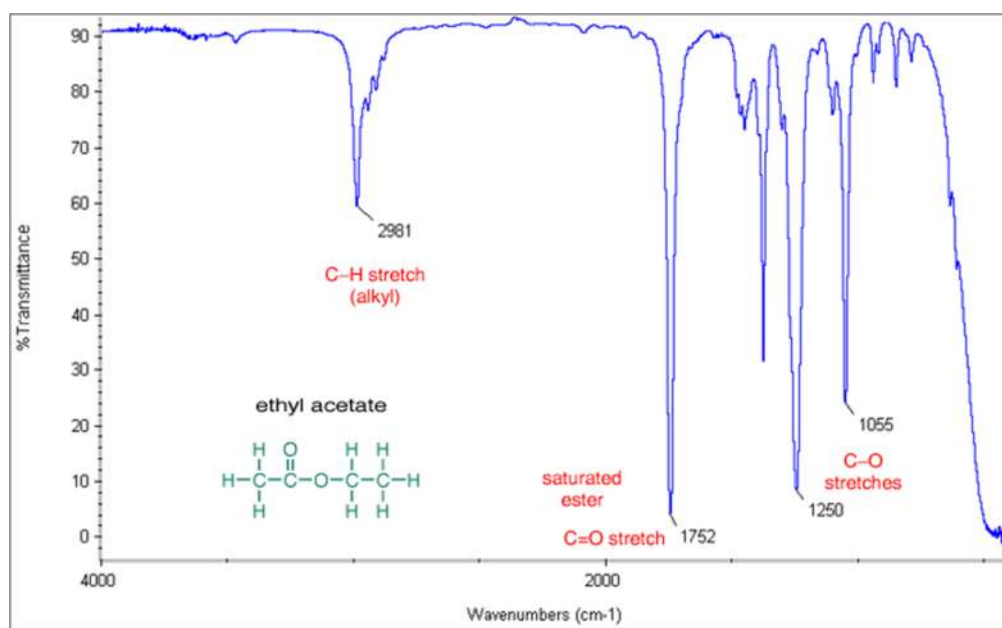
- **Cannot be used on patients with metal in them (pacemakers, implants etc)**
- **Machines are costly.**

57. Combining NMR, Infrared Spectroscopy and Mass Spectrometry.

(i) analyse infrared absorptions in an infrared spectrum to identify the presence of functional groups in a molecule (see also unit F322: 2.2.3.b),

**This was covered in the module F322, for more detail see the previous revision list.**

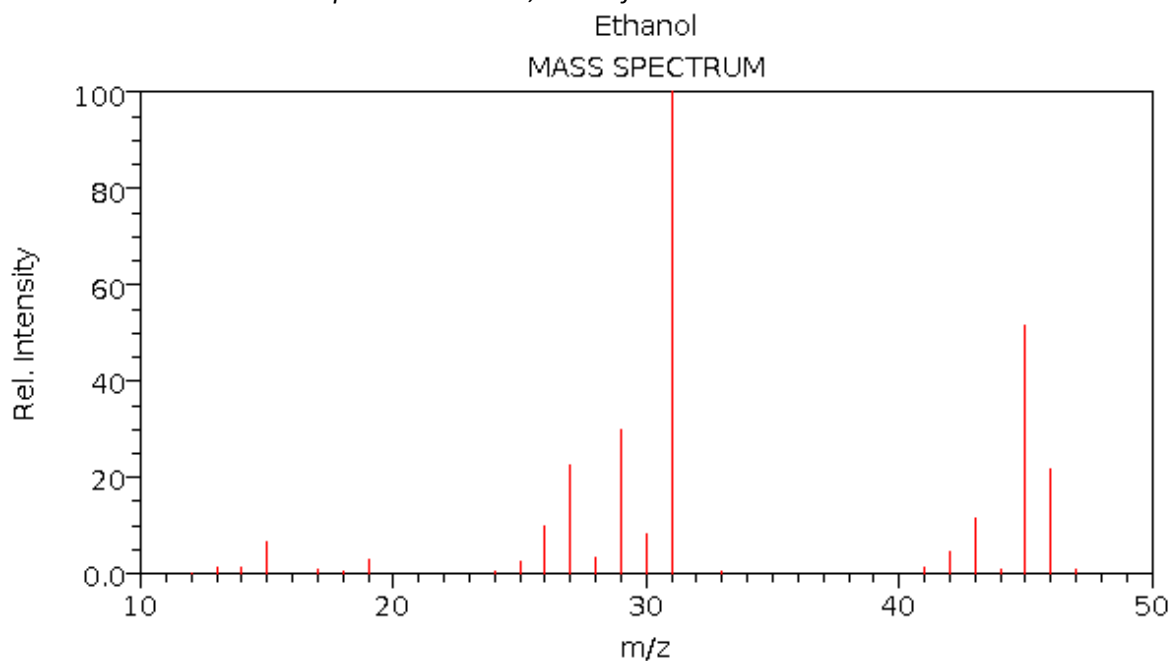
**Infrared can be used to determine which functional groups are in a molecule, however different homologous series' have the same functional groups so, on its own, it is not completely effective.**



**You can identify the functional groups by looking at the wavenumbers and the breadth of each peak.**

(ii) analyse molecular ion peaks and fragmentation peaks in a mass spectrum to identify parts of structures (see also unit F322: 2.2.3.f–h),

This was also covered in the previous module, so see for more details.



***This type of analytic technique can provide a percentage by mass of each element. The empirical formula can then be derived from this.***

***However it tells you nothing about the structure of the molecule, and also there may be other compounds with the same molecular formula.***

***These analytical techniques can all be combined together to all give separate hints as to what a compound may be. This can make it easier for chemists to deduce the actual formula of a compound.***