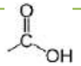
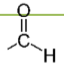
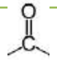
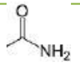
Unit 1a: Intro - Nomenclature

1. Keywords

Functional group:	an atom, or a group of atoms that has similar chemical properties whenever it occurs in different compounds. It defines the characteristic physical and chemical properties of families of organic compounds.
Homologous series	A series of related chemical compounds that have the same functional group(s) but differ in formula by CH_2
Isomer	two or more compounds with the same molecular formula but different arrangement of atoms

2. Functional groups.

Homologous series	Prefix or suffix	Functional group
Alkane	-ane	C—C
Alkene	-ene	C=C
Alcohol	hydroxy-/-anol	-OH
Carboxylic acid	-anoic acid	
Haloalkane	Chloro- Bromo- Iodo-	-Cl -Br -I
Aldehyde	-anal	
Ketone	-anone	
Amine	Amino-/-ylamine	-NH
Nitrile	Cyano-/-nitrile	-CN
Amide	-anamide	

3. International Union of Pure and Applied Chemistry (IUPAC) rules

1. Identification of the longest "parent" hydrocarbon chain
2. Identification of the side-chains branching off the parent one, the prefixes
3. Numbering of the chain. So that the functional group with the highest precedence has the lowest possible number, OR side chains have lowest possible number
4. If there is more than one of the same alkyl group substituent then indicate this by using di, tri or tetra
5. Use a hyphen between letters and numbers and a comma between two numbers
6. Different side-chains and functional groups will be grouped together in alphabetical order. The prefixes di-, tri-, etc. are not taken into consideration for grouping alphabetically
7. Identification any suffixes needed due to the functional group
8. Number the position of the functional group if needed
9. Show a double bond in addition to the functional group by changing 'an' to 'en'

Number of C atoms	1C	2C	3C	4C	5C	6C	7C	8C	9C	10C
prefix	Meth-	Eth-	Prop-	But-	Pent-	Hex-	Hept-	Oct-	Non-	Dec-

Order of precedence of groups:

Carboxylic acid > Ester > Acyl Chloride > Amide > Nitrile > Aldehyde > Ketone > Alcohol > Amine

4. Cahn-Ingold-Prelog (CIP) rules

These rules help with naming geometric isomers E/Z:

1. Compare the atomic number of the atoms directly attached to the right-hand carbon of the double bond; the group having the atom of higher atomic number receives higher priority.
2. If there is a tie, we must consider the atoms one bond further away and repeat until we have an atom of higher atomic number.
3. Repeat with the atoms directly attached to the left-hand carbon of the double bond.

E: the higher priority groups are on opposite sides of the double bond.
Z : the higher priority groups are on the same side of the double bond.

5. Features of a homologous series

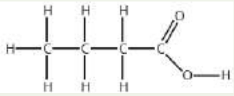
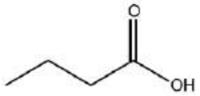
Can be represented by a general formula
Show a gradual change in physical properties
Differ by CH_2
Same chemical properties
Same functional group

Unit 1b:Intro- Spacial representation

1. Useful terms used throughout the course (not all needed in unit 1)

Addition	reaction where two or more molecules combine to form a single molecule $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$
Combustion	reaction with oxygen to release heat and light $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$
Condensation	reaction in which two or more molecules combine to form a larger molecule, with the simultaneous loss of a small molecule such as water, ammonia or hydrogen chloride. The H is removed from an oxygen or nitrogen $CH_3NH_2 + CH_3COOH \rightarrow CH_3NHCOCH_3 + H_2O$
Decomposition	the breakdown of a single substance into two or more species $2H_2O_2 \rightarrow 2H_2O + O_2$
Dehydration	reaction that involves the loss of water. The H is removed from a carbon $C_2H_5OH \rightarrow C_2H_4 + H_2O$
Elimination	produces an unsaturated product by loss of atoms or groups from adjacent carbon atoms. Dehydration is a specific type $C_2H_5OH \rightarrow C_2H_4 + H_2O$
Hydration	the addition of water to a molecule $C_2H_4 + H_2O \rightarrow C_2H_5OH$
Hydrocarbon	a chemical containing ONLY hydrogen and carbon atoms
Hydrolysis	splitting a substance by the addition of water $CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$
Neutralisation	reaction in which an acid and a base react to produce a salt and water $NaOH + HCl \rightarrow NaCl + H_2O$
Redox	reaction where reduction and oxidation happen simultaneously $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
Saturated	a chemical containing only single bonds C-C bonds
Substitution	reaction during which one atom or group of atoms in a single substance is replaced by another. $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
Unsaturated	a chemical containing at least one C=C double bond

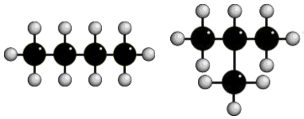
2. Types of chemical formulas

Molecular Formula	shows the actual number of atoms of each element in a molecule.	$C_4H_8O_2$
Empirical Formula	the simplest ratio of the atoms of each element present in a compound (always in order CH and then alphabetical)	C_2H_4O
Structural Formula	show the atoms carbon by carbon without showing any of the bonds, giving the minimum detail needed to be unambiguous	CH_3CH_2COOH
General formula	an algebraic formula that can describe any member of a family of compounds	$C_nH_{2n+1}COOH$
Displayed Formula (drawn)	shows every atom and every bond	
Skeletal Formula (drawn)	for the C-H backbone shows only the bonds, otherwise shows atoms and bonds	

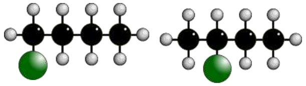
STRUCTURAL ISOMERISM

Same molecular formula but different structural formulae

CHAIN ISOMERISM



POSITION ISOMERISM



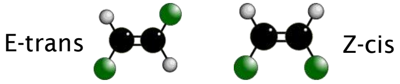
FUNCTIONAL GROUP ISOMERISM

STEREOISOMERISM

Same molecular formula but atoms occupy different positions in space.

GEOMETRICAL ISOMERISM

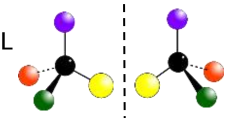
Occurs due to the restricted rotation of C=C double bonds (E/Z or trans/cis)



OPTICAL ISOMERISM

Occurs when molecules have a chiral centre. Get two non-superimposable mirror images.

Two options R/L



Unit 2a: Alkanes

1. Properties

General formula: C_nH_{2n+2}
Saturated hydrocarbons
Properties are linked to the length of their chains.

Chain length	Short	Long
Boiling point	Low	High
Flammability	High - Ignites easily	Low -Hard to ignite
Viscosity	High - Flows easily	Low - Doesn't flow well

Between the molecules there are weak intermolecular forces of attraction which increase with the chain length.
Alkanes are fairly unreactive but burn well so used as fuels

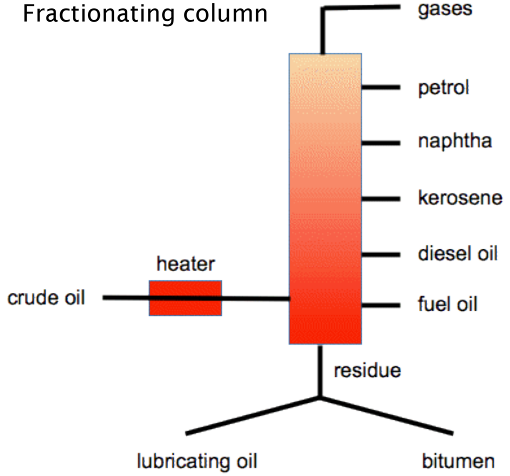
2. Fractional distillation

Petroleum (also called crude oil) is a mixture of mainly alkane hydrocarbons that can be separated by fractional distillation

- crude oil heated to vaporise it and fed into the bottom of a fractionating column, hottest at bottom, coolest at top.
- the vapours pass up the tower to the point where it is cold enough to allow their condensation depending on boiling point.
- at each level the fraction (a group of hydrocarbons of similar chain length, with similar boiling points) is piped of.
- lighter chains rise, cool and condense at the top
- heavier chain fractions are collected at the bottom

Large chain fractions are cracked producing smaller more useful fuels.

Fractionating column

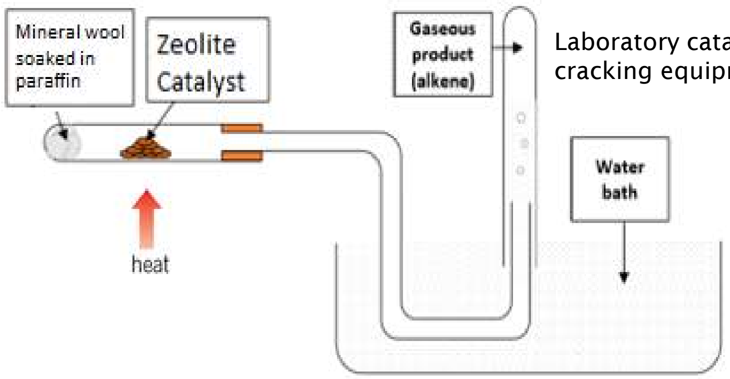


3. Cracking

Cracking – long chain hydrocarbons are broken down randomly into short chain hydrocarbons
Done to produce substances which are more in demand, and in short supply, with a higher value

Thermal cracking
Conditions high temperature and high pressure
High proportions of alkenes are produced.

Catalytic cracking
Conditions high temperature, pressure just above atmospheric and zeolite catalyst. Used to make motor fuels. Makes branched alkanes, cycloalkanes and aromatic compounds.



Laboratory catalytic cracking equipment

4. Combustion

- Complete combustion (excess oxygen) of alkanes produces carbon dioxide and water only.
  Releases large amounts of energy.
  Blue Bunsen flame
- Incomplete combustion (limited supply of oxygen) of alkanes produces carbon monoxide and water, with even less oxygen carbon (soot) is produced.
  This often happens with long hydrocarbons that need a lot of oxygen.
  Less energy is released.
  Yellow Bunsen flame

Unit 2b: Pollution

1. Pollution

unburnt hydrocarbons	unburnt petrol or diesel	photochemical smog, greenhouse gases
carbon	incomplete combustion of fuel	respiratory problems for humans, asthma and cancer
carbon monoxide (CO)	incomplete combustion of fuel	toxic to humans
carbon dioxide (CO_2)	complete combustion of hydrocarbon fuels	greenhouse effect
nitrogen oxides (NO_x)	combustion of nitrogen from air, usually in car engines at high temperatures $N_2(g) + O_2(g) \rightarrow 2NO(g)$	acid rain, smog
sulfur dioxide (SO_2)	combustion of sulfur impurities in petrol $S(s) + O_2(g) \rightarrow SO_2(g)$ $SO_2\ (s) + \frac{1}{2}\ O_2(g) + H_2O(l) \rightarrow H_2SO_4(l)$	acid rain
water (H_2O)	combustion of hydrocarbon fuels	greenhouse effect

3. Catalytic converter

The catalytic converters is a honeycomb made of ceramic coated with platinum and rhodium metals that work as catalysts. The structure allows for a high surface area to catalyse:

$$2CO\ (g) + 2NO\ (g)) \rightarrow CO_2\ (g) + N_2(g)$$

And this reaction with unburned hydrocarbons (make sure to balance it):

$$C_xH_y + NO \rightarrow N_2 + H_2O + CO_2$$

2. Desulfurisation

The gases given out by power stations are called flue gases so the process of removing sulphur dioxide is called flue gas desulfurisation.

$CaO + SO_2 \rightarrow CaSO_3$

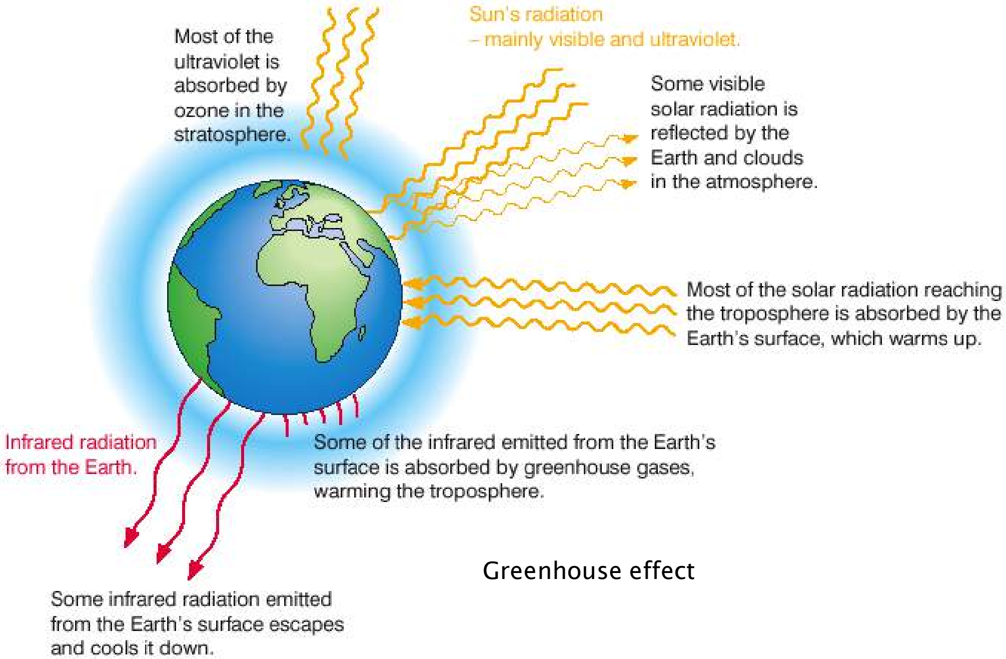
and $CaSO_4 + 2H_2O + {}^1/_2O_2 \rightarrow CaSO_4.2H_2O$

$CaSO_3$ is calcium sulfite

$CaSO_4.2H_2O$ is gypsum

If calcium carbonate is used:

$CaCO_3 + SO_2 + {}^1/_2O_2 \rightarrow CaSO_4 + CO_2$



Greenhouse effect

Unit 2c: Chlorination

1. Keywords

Mechanism	a series of steps showing electron movement
	two electrons moving
	one electron moving
Initiation:	radical forming step
Propagation:	steps which use up AND regenerate radicals
Termination:	a step which removes radicals
Free radical:	a very reactive chemical species with an unpaired electron

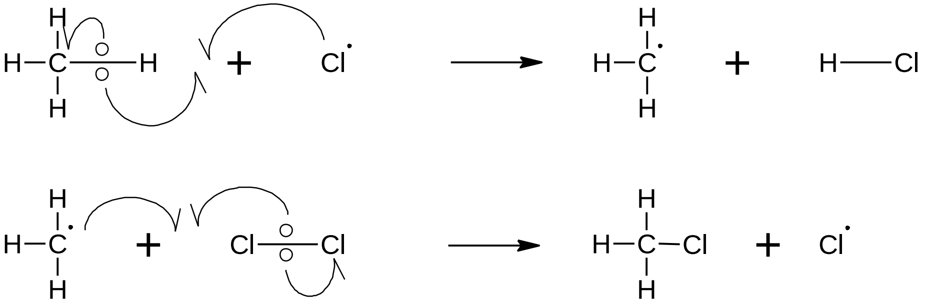
2. Free radical substitution to chlorinate alkanes

Example reaction: $CH_{4(g)} + Cl_{2(g)} \rightarrow CH_3Cl_{(g)} + HCl_{(g)}$
This reaction occurs only in the presence of UV light.

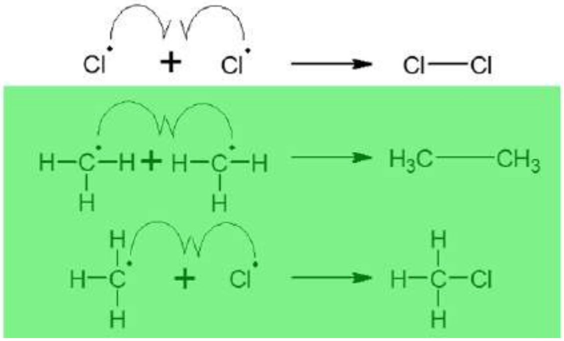
Initiation

$$Cl{-}Cl \longrightarrow Cl^{\bullet} + Cl^{\bullet}$$

Propagation



Termination

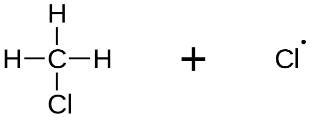


This gets recycled

This is an impurity

This is the required product

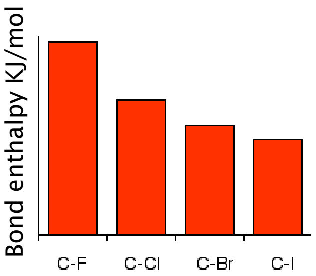
Chain reaction
The reaction can continue to give multiple substitutions and a mixture of products

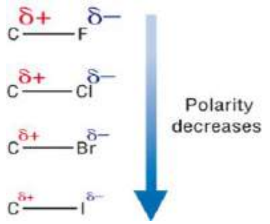


Unit 3: Halogenoalkanes

1. Keywords

Anhydrous	in the absence of water
Nucleophile	electron pair donor
R group	a simplified way of saying a formula could contain an H atom or carbon chain
Reflux	to heat with a vertical condenser so the mixture continuously evaporates and condenses. It is used when heating flammable chemicals and those with very low boiling points





2. Properties

General formula $C_nH_{2n+1}X$ where X is the halogen

Halogenoalkanes can be classified into:
- Primary have one R group attached to the carbon linked to the halogen.
- Secondary have two R groups attached to the carbon linked to the halogen.
- Tertiary have three R groups attached to the carbon linked to the halogen.

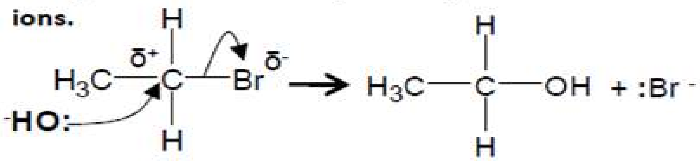
Physical properties of halogenoalkanes mainly depend on the polarity of the C-X bond.
- Solubility: the polarity of the bond is not enough to make halogenoalkanes soluble in water, the main intermolecular forces are Van der Waals and dipole-dipole attractions.
- Boiling point: - increases with increased chain length.
  - increases going down the halogen group.

Chemical properties depend on the C-X bond strength and polarity. Reactivity increases going down the halogen group even though C-I is the least polar bond, this is due to atom size resulting in a longer weaker bond

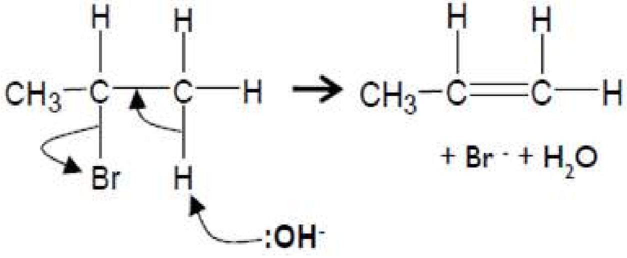
3. Chemical reactions

Nucleophilic substitution: OH^-, CN^-, NH_3
OH^-: warm, aqueous alkali. The alkali and halogenoalkane don't mix, the reaction only happens where the two layers meet.
CN^-: reflux with ethanolic KCN, extra step to reform nucleophile
NH_3: warm, excess ethanolic ammonia, sealed tube, ammonium salt formed, extra step to remove additional H^+, can get mixture of products from multiple substitutions

Halogenoalkanes with aqueous hydroxide ions.



Elimination: reflux with aqueous alkali, ethanol solvent



4. Concurrent elimination and substitution

Condition	**Reaction type**
Water is solvent	Mainly Substitution
Increasing ethanol concentration	Increases elimination
Warm	Mainly substitution
Reflux	Mainly elimination
Primary halogenoalkane used	Mainly substitution
Secondary halogenoalkane used	Both
Tertiary halogenoalkane used	Mainly elimination

4. CFCs

Chlorofluorocarbons (CFCs) can be damaging for the ozone layer due to a free radical mechanism reaction where chlorine acts as a catalyst to the breakdown of ozone into oxygen.

$CCl_2F_2 \rightarrow {}^\bullet CClF_2 + Cl^\bullet$
$Cl^\bullet + O_3 \rightarrow ClO^\bullet + O_2$
$ClO^\bullet + O_3 \rightarrow Cl^\bullet + 2O_2$

Unit 4: Alkenes

1. Keywords

Carbocation	ion with a positively charged carbon atom
Electrophile	an electron pair acceptor
Repeat unit	the simplified version of the polymer which just shows the part that is repeated over and over again
Plasticiser	a small chemical which when mixed with a monomer makes the polymer more flexible

2. Properties

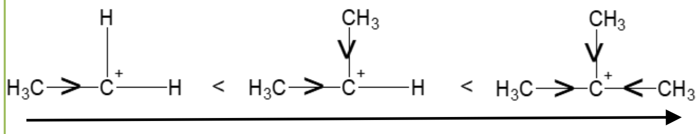
General formula C_nH_{2n}

Functional group is the C=C double bond which consists of a σ bond and a π bond.

- π bond lies above and below the σ bond.
- There is no rotation around a double bond – resulting in geometric isomers (cis/trans E/Z)
- The double bond sits on a plane and the angles between each bond is 120°

Double bond is an electron rich area which can easily attract electrophiles

4. Unsymmetrical addition



Increasing stability due to positive inductive effect.

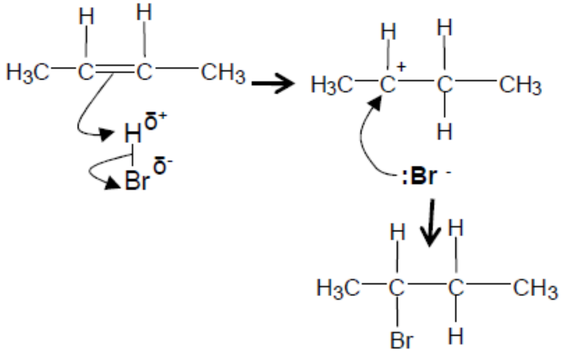
The more stable the carbocation is, the more likely it will be formed in the reaction and therefore the more likely that product.

3. Chemical Reactions

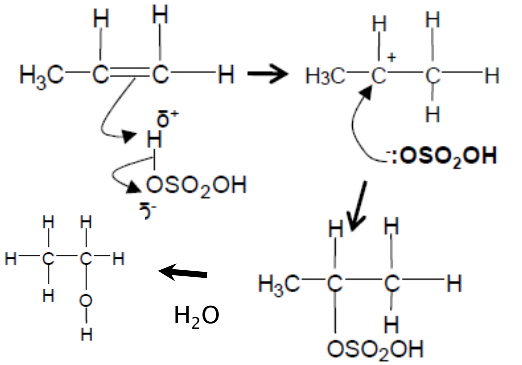
- Combustion – alkenes will burn in oxygen like alkanes.

- Electrophilic additions reactions
- Hydrogenation: with hydrogen and a finely divided nickel catalyst 150℃. Makes alkanes
- With steam: phosphoric acid catalyst. High T and P. Makes alcohols
- With halogens: room temperature. Makes dihalogenoalkanes. The reaction with bromine water is test for alkenes: orange solution goes colourless.
- With hydrogen halides: room temperature. Makes halogenoalkanes
- With sulfuric acid: room temperature. Makes an alcohol.

Electrophilic Addition of Alkenes with hydrogen bromide

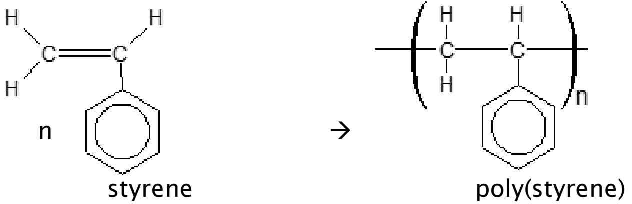


Electrophilic Addition of Alkenes with sulphuric acid



- Polymerisation

Addition polymers are unreactive due to single C-C bonds



PVC: poly(chloroethene)- closed packed chains, rigid; used for drainpipes and window frames
Plasticised PVC- flexible; used for wiring insulation and clothing

Chain length: long chains = strong, more entangled and stronger intermolecular forces
Side groups: polar side groups allow stronger intermolecular forces
Branching: straight chains pack closer so stronger intermolecular forces than branched
Stereoregularity: regular arrangement allows closer packing so stronger intermolecular forces
Chain flexibility: rigid chains make strong polymers, hydrocarbon polymers have many rotatable bonds so are flexible, benzene rings make the chains rigid

Unit 5: Alcohols

1. Keywords

Carbon neutral	No net carbon dioxide emission into atmosphere
Biofuel	A fuel produced from renewable biological resources e.g plants

2. Properties

General formula $C_nH_{2n+1}OH$

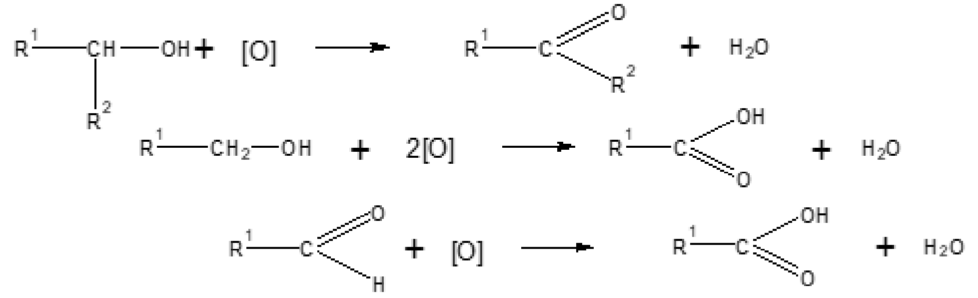
- Classified as primary, secondary and tertiary
- The –OH group allows alcohols to form hydrogen bonds.
- Short alcohols are soluble in water

3. Production of ethanol

	Hydration of ethene	Fermentation of sugars
Equations	$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$	$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$
Conditions	High T and P, H_3PO_4 catalyst	Yeast, 25-42°C, anaerobic, neutral pH, aqueous glucose
Sustainability	Non-renewable	Renewable
Plant costs	High	Low
Rate of reaction	Fast	Slow
Production type	Continuous	Batch
Purity	Approx 100%	Low, must be distilled
Yield	Approx 100%	Approx 15%
Atom economy	100%	51%
Energy use	High	Low
Carbon neutral	No	Yes, if farming processes ignored $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ $2C_2H_5OH + 6O_2 \rightarrow 6H_2O + 4CO_2$
Environmental impacts	Use of crude oil, CO_2 released in energy production	Deforestation, loss in biodiversity, CO_2 released

4. Oxidation

Reagent	Oxidising agent	Conditions	Product
1° alcohol	Acidified dichromate: H_2SO_4 and $K_2Cr_2O_7$	Warm, excess alcohol, distil off as soon as formed	Aldehyde
1° alcohol		Reflux, excess [O]	Acid
2° alcohol		Reflux	Ketone
aldehyde		Reflux	Acid

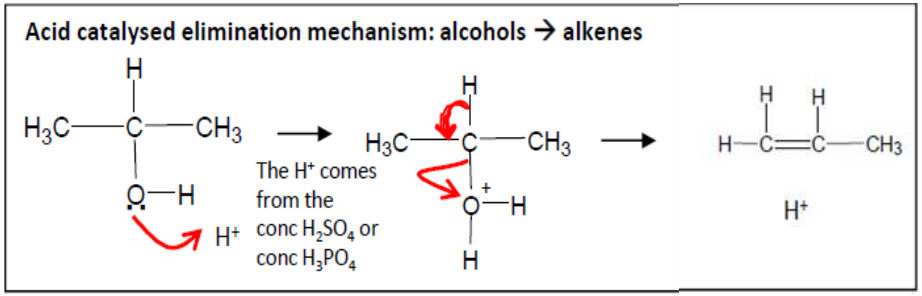


Testing product for aldehyde or ketone	
	Fehling's, warm. Blue to brick red ppt (Cu_2O)
	Tollens', warm. Silver mirror on tube (solid silver)

5. Elimination

Dehydration reaction
High T and concentrated sulphuric acid catalyst

An alkene is formed.



Acid catalysed elimination mechanism: alcohols → alkenes

Unit 6: Organic analysis

1. Reactions

Functional group	Reagent	Result
Alkene	Bromine water	Orange to colourless
1° or 2° alcohol	Sodium dichromate and sulfuric acid	Orange to green
Aldehyde	Fehling's solution	Blue solution to red ppt
	Tollens' reagent	Silver mirror formed
	Sodium dichromate and sulfuric acid	Orange to green
Carboxylic acid	Sodium carbonate $2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2Na + H_2O + CO_2$	Bubbles of CO_2 evolved
	pH paper/indicator	Mildly acidic solution

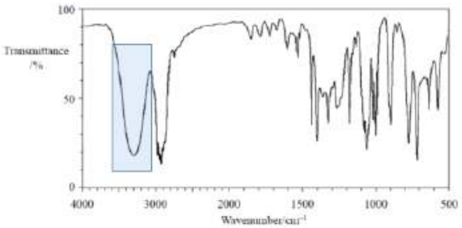
5. Infra red

- Infrared radiation is absorbed by bonds making them vibrate.
- Different bonds absorb IR radiation at different wavelengths and can be used to identify different functional groups.

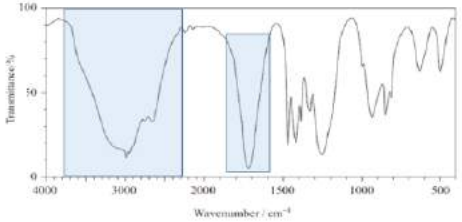
- The fingerprint region is in the range 1500-500cm^{-1} is too complicated to analyse.
- Because the fingerprint region is unique, compounds can be identified by comparing it to a data base of known IR spectra.

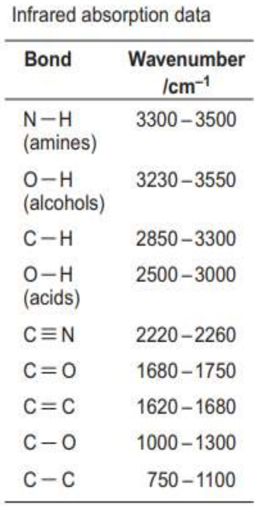
- IR only gives information about functional groups. Other evidence is required to find the precise structural formula.

OH Alcohols 3230 – 3550 cm^{-1}



OH carboxylic acid 2500 – 3000 cm^{-1}
C=O 1680 – 1750 cm^{-1}





Infrared absorption data

Bond	Wavenumber /cm^{-1}
N–H (amines)	3300 – 3500
O–H (alcohols)	3230 – 3550
C–H	2850 – 3300
O–H (acids)	2500 – 3000
C≡N	2220 – 2260
C=O	1680 – 1750
C=C	1620 – 1680
C–O	1000 – 1300
C–C	750 – 1100

3. Tollens' Reagent

- Reagent: aqueous ammonia + silver nitrate.
- The active substance is the complex ion of $[Ag(NH_3)_2]^+$
- Conditions: heat in water bath
- Reaction: silver(I) ions reduced to silver atoms; aldehydes/alcohols oxidised.
- Observation: a silver mirror inside the tube. Ketones result in no change.

$$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$$

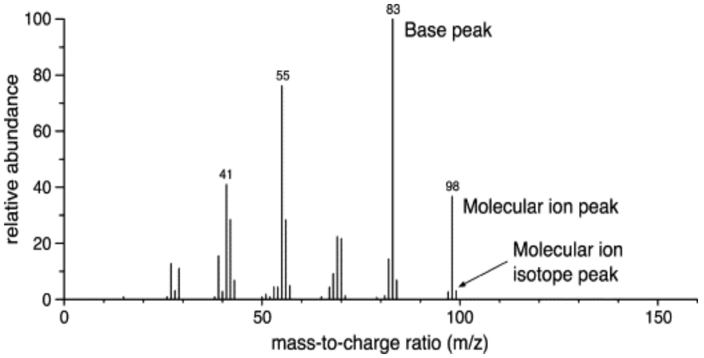
4. Fehling's Solution

- Reagent: Fehling's Solution containing blue Cu^{2+} ions.
- Conditions: heat in water bath
- Reaction: aldehydes are oxidised; Cu^{2+} reduced to Cu^+
- Observation: Blue Cu^{2+} ions in solution change to a red precipitate of Cu_2O. Ketones result in no change.

$$CH_3CHO + 2Cu^{2+} + 2H_2O \rightarrow CH_3COOH + Cu_2O + 4H^+$$

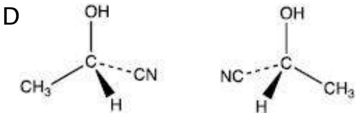
6. Mass Spectrometry

- Base peak: most abundant
- Molecular ion: gives Mr of molecule
- Small peaks to right of molecular ion due to elemental isotopes
- Peaks to left of base peak due to fragments
- High resolution mass spec has values to 4 d.p so can distinguish between molecules with same Mr but different elements



Unit 7: Optical isomerism

Keywords

Chiral centre	A carbon attached to four different groups, also called an asymmetric carbon
Racemate	A mixture of equal amounts of two optical isomers
Enantiomer	An individual optical isomer, one of a pair of mirror images; they differ only in their effects on plane polarised light
Chirality	The property where a molecule can exist as two non-superimposable mirror images
Optical isomerism	A form of stereoisomerism which occurs as a result of chirality in molecules
Optically inactivity	Happens when you have a racemate and the rotations caused by each enantiomer cancel out
Show all 3 types of bond in 3D Draw as mirror images The two bonds drawn in the same way must be adjacent	

Unit 8: Aldehydes and ketones

1. Nomenclature

The carbonyl group is present in aldehydes (RCHO) and ketones (RCOR').
They are both represented by the general formula $C_nH_{2n}O$.

- Aldehydes (-al suffix) can only be at the end of a molecule so there is no need to provide numbering their functional group.
- No ketone (-one suffix) can have less than 3 carbons. So you don't need to number the carboxyl group in propanone or butanone

- Bond angle of C=O is 120

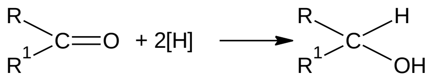
2. Physical properties

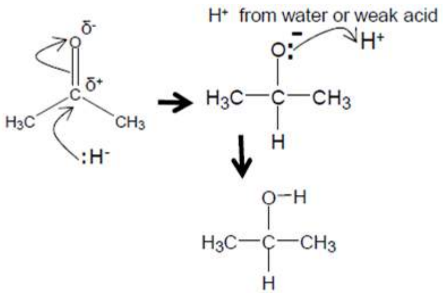
The big difference in **electronegativity** between carbon and oxygen, makes the C=O bond strongly polar**.**
There are permanent **dipole-dipole** forces between the molecules.

Shorter chains carbonyl compounds are readily soluble in water since they form hydrogen bonds with water. As the aryl/alkyl chain lengthens solubility decreases.

4. Reactivity

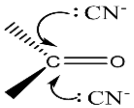
Reduction: nucleophilic addition to form alcohols
Reducing agent: sodium tetrahydridoborate(III) ($NaBH_4$)
Nucleophile: H- (hydride ion)

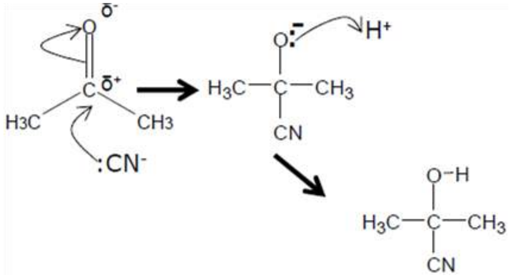




Nucleophilic addition to form hydroxynitriles:

- KCN followed by addition of dilute hydrochloric acid generates the HCN needed
- The reaction is very important since it increases the length of the carbon chain by one carbon.
- KCN toxic but relatively safe BUT when the acid is added some toxic HCN gas may be formed so needs a fume cupboard
- Flammable reactants so use water bath
- Nucleophilic attack can be above or below plane of C=O so aldehydes and unsymmetrical ketones give a racemate





Oxidation:
Aldehydes can be oxidised to carboxylic acids.

Unit 9a: Carboxylic acids and esters

1. Keywords

Delocalisation:	when electrons not associated with a single atom or a covalent bond, providing stabilisation

2. Carboxylic acids

Carboxylic acids (RCOOH) have two functional groups:

Carboxyl group Hydroxyl group

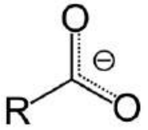
Nomenclature:

- Suffix: -oic acid
- The functional group always ends the chain and is included in carbon chain of the root name if the acid is not attached to a benzene ring
- Numbering starts from the carboxyl –COOH carbon

Physical properties:

- Acids form hydrogen bonds so have higher boiling points than the respective alkanes.

Reactivity:



- Due to the stability of the carboxylate ion caused by delocalisation of its charge across three atoms, the –OH group in acids is more acidic than alcohols, carboxylic acids are weak acids, so they form an equilibrium when they dissociate
- They undergo the same chemical reactions as any inorganic acid acting as proton donors e.g., liberation of CO_2 from carbonates
- React with alcohols using an acid catalyst to form esters

3. Esters

Nomenclature:

- The name of the esters are based on that of the parent acid but the name always begins with the alkyl or aryl group that has replaced the hydrogen of the acid;

  i.e. methanol + ethanoic acid → methyl ethanoate

Physical properties:

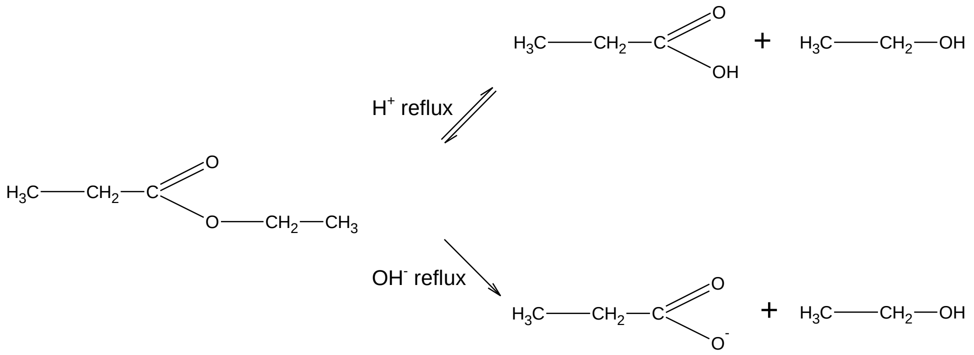
- Short esters are volatile and have pleasant fruity smells and are used in perfumes or as flavourings.
- They are also use as solvent and plasticisers.

Reactivity:

- Hydrolysis to acid and alcohol:

❖ Acidic: can occur at room temperature with a strong acid as a catalyst, the reaction does not go to completion.

❖ Base: in the presence of a base the salt of the acid is produced, and the reaction goes to completion. The acid can be liberated by adding an inorganic acid

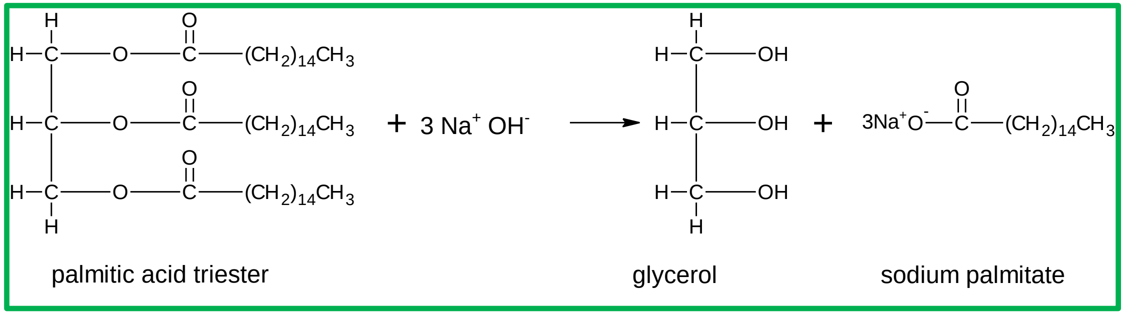


Biodiesel:

- A mixture of methyl esters of long-chain carboxylic acids.
- Produced by reacting vegetable oils with methanol in the presence of a catalyst.

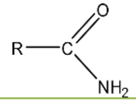
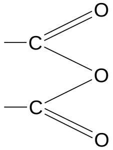
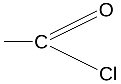
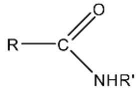
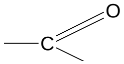
4. Triglycerides (animal fats and vegetable oils)

- Triglycerides are esters of the alcohol propane-1,2,3-triol (glycerol) and “fatty acids” which are long chained (12-18) carboxylic acids.
- Fats are unsaturated and solid, vegetable oils are saturated and liquids.
- Fats and oils can be hydrolysed by boiling in NaOH – making glycerol and a mixture of sodium salts. The salts are called soap and are used as cleaning agents.

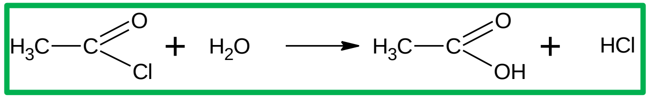
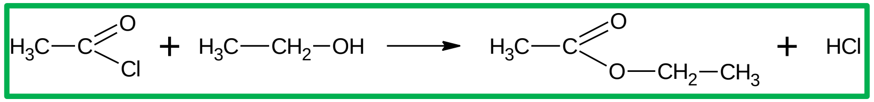
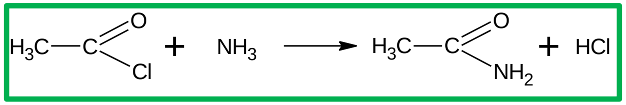
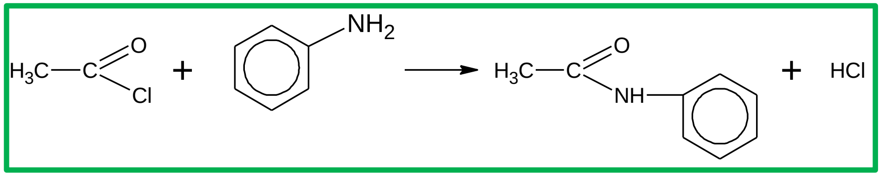


Unit 9b: Acylation

1. Keywords

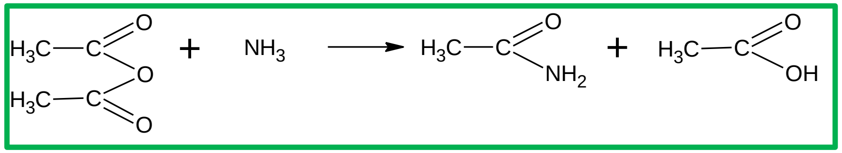
Acid derivative	A molecule where the acid –OH has been replaced by another functional group that is not a H or a carbon chain.
Amide	
Acid anhydride	
Acyl chloride	
N-substituted amide	
Acylation	A reaction where an acyl group is added to a molecule
Acyl group	

2. Acylation (Addition- elimination reaction)

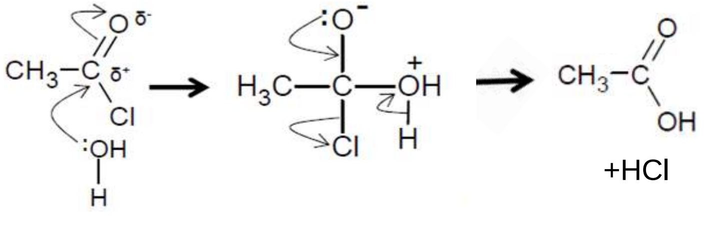
Nucleophile	Equation	Notes
water		Vigorous with cold water, white misty fumes seen
alcohol		Vigorous at room temperature, white misty fumes seen, fruity smell
ammonia		Violent at room temperature, dense white solid smoke seen
1° amine		Violent at room temperature, dense white solid smoke seen

Ethanoic anhydride is used as an acylating agent over ethanoyl chloride during most reactions including aspirin manufacture:

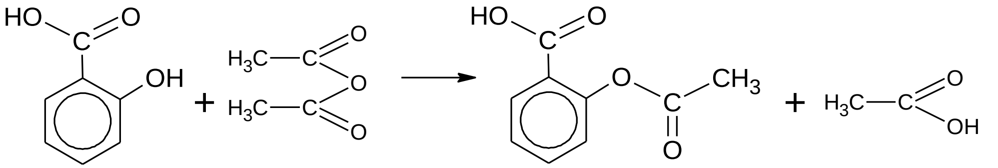
- It is cheaper
- It is less corrosive
- It is safer as the by-product is ethanoic acid rather than hydrogen chloride.



3. Nucleophilic addition –elimination mechanism



4. Aspirin production



Unit 10: Aromatic chemistry

1. Structure and bonding

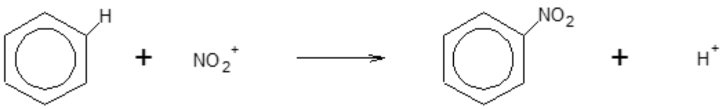
Stage 1 Bonding
1a) Each C has three (covalent) bonds
1b) Spare electrons (in a p orbital) overlap (to form a π cloud)
1c) Delocalisation

Stage 2 Shape
2a) Planar
2b) Hexagon/6 carbon ring/120° bond angle
2c) C–C bonds equal in length / C–C bond lengths intermediate between single and double bond

Stage 3 Stability
3a) Expected ΔH^o hydrogenation of cyclohexatriene = –360 kJ mol^{-1}
3b) ΔH^o hydrogenation benzene (is less exothermic) by 152 kJ mol^{-1}
3c) Benzene lower in energy than cyclohexatriene / Benzene is more stable due to delocalisation

2. Benzene – Electrophilic substitution

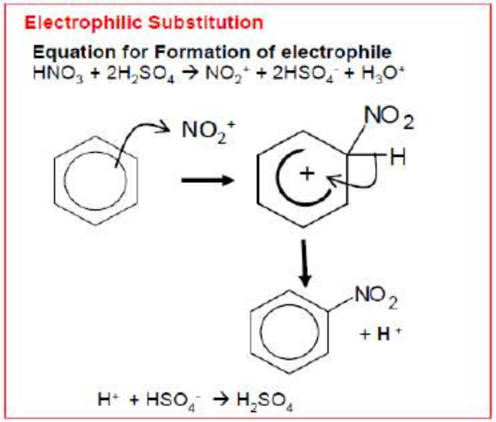
Nitration
Overall reaction:



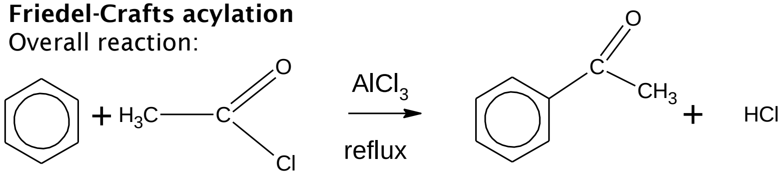
Electrophile: NO_2^+ formed from concentrated nitric acid and concentrated sulfuric acid.

$$2H_2SO_4 + HNO_3 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

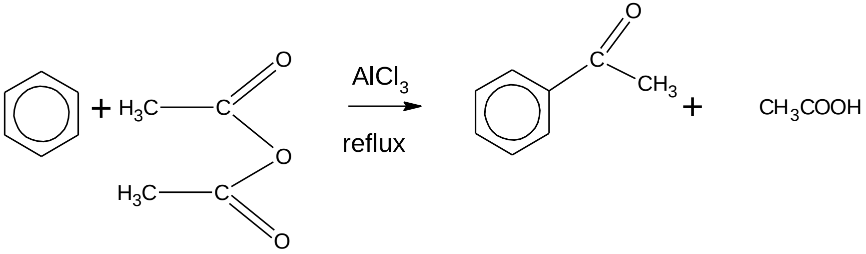
Conditions: 50-60°C, any higher gives multiple substitutions; conc. sulfuric acid is the catalyst
Uses: Nitrobenzenes have many uses in the manufacture of both dyestuffs and chemicals such as amines.
Multiple substituted benzenes tend to be explosive.



Friedel-Crafts acylation
Overall reaction:



ethanoyl chloride



ethanoic anhydride

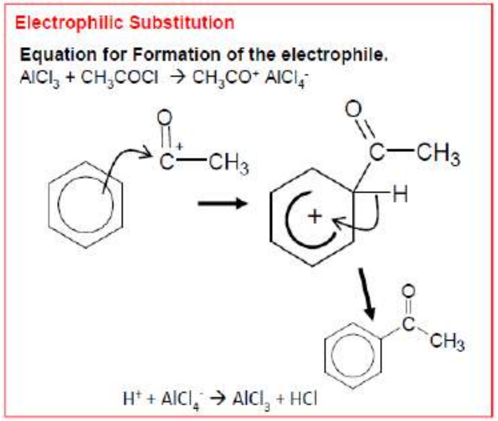
Electrophile RCO+ formed from reaction of acid derivative with $AlCl_3$

$$RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$$

Conditions: reflux, $AlCl_3$ acts as a catalyst and is reformed by reacting with H^+ from the benzene ring:

$$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$$

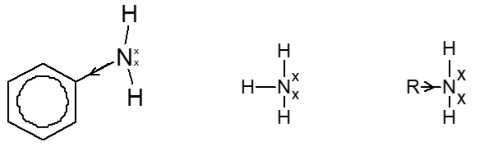
Uses: Important step in many organic synthesis reactions



Unit 11: Amines

1. Amines as bases

- Aromatic amines are weak bases because the nitrogen lone pair is drawn into the benzene delocalisation so the electron density on the N lowers.
  The lone pair is less available to accept a proton.
- Aliphatic amines are strong bases because the alkyl group has an inductive effect which pushes electrons towards the nitrogen, increasing electron density of the N.
  The lone pair is more available to accept a proton.



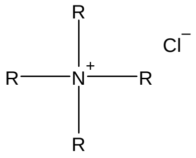
$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$

3. Acting as nucleophiles

Reaction of ammonia or amines with halogenoalkanes (Nucleophilic substitution)

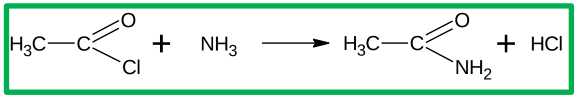
The reaction to prepare amines can also be thought of as the amine acting as a nucleophile in a substitution with a halogenoalkane.

Every hydrogen and the lone pair on the nitrogen of the NH_2 can be substituted with the halogenoalkane producing a mixture of 1° amine, 2° amine, 3° amine and the quarternary ammonium salt

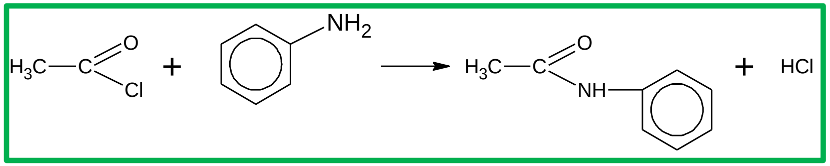


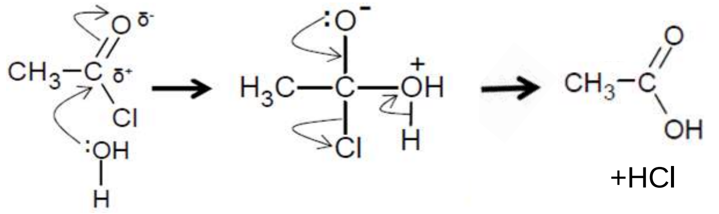
quarternary amine

Nucleophilic addition-elimination



Both violent at room temperature, dense white solid smoke seen

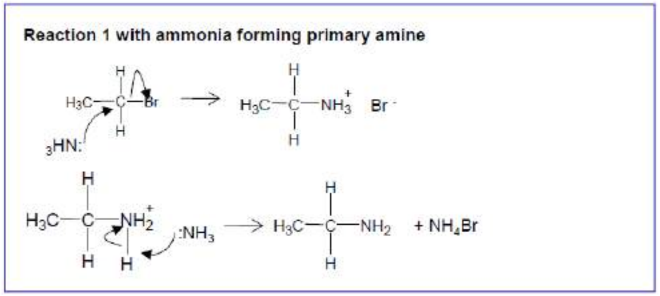


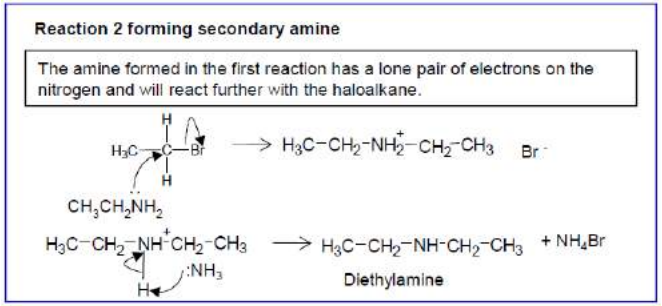


2. Preparation

Reaction of ammonia with halogenoalkanes (Nucleophilic substitution)

NH_3: warm, excess ethanolic ammonia, sealed tube, ammonium salt formed, extra step to remove additional H^+, can get mixture of products from multiple substitutions





The amine formed in the first reaction has a lone pair of electrons on the nitrogen and will react further with the haloalkane.

Reduction of nitriles

Halogenoalkanes react with a cyanide ion in aqueous ethanol. The ion replaces the halide ion by nucleophilic substitution to form a nitrile.

$$RBr + CN^- \longrightarrow R{-}C{\equiv}N + Br^-$$

Nitriles can be reduced to primary amines with a nickel/hydrogen catalyst.

$$R{-}C{\equiv}N + H_2 \longrightarrow R{-}CH_2NH_2$$

Reduction of nitro compounds

Electrophilic substitution (nitration) of benzene.

Nitrobenzene reduced to phenylamine using tin and HCl as the reducing agent

$$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$$

The amine formed reacts with the acid used to produce a soluble salt

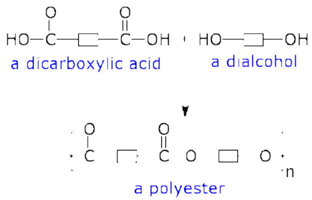
Aromatic amines are used to manufacture dyes

Unit 12: Polymers

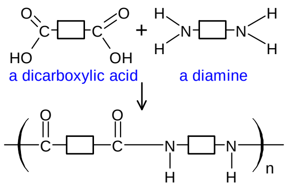
1. Condensation polymers

Condensation polymerisation

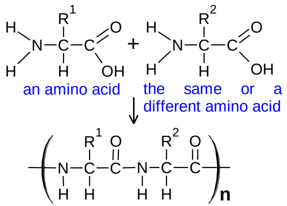
- Condensation polymerisation involves monomers with two functional groups (COOH and OH or COOH and NH_2groups)
- During the condensation water or other small molecules are eliminated
- Common condensation polymers: - Polyesters (-COO- ester linkage), like Terylene
  - Polyamides (-CONH- amide linkage), like Nylon and Kevlar
  - Polypeptides (-CONH- peptide linkage), all proteins.



a polyester



a polyamide

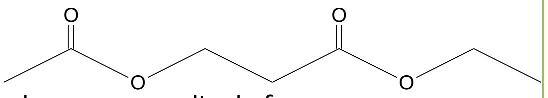


a polypeptide or protein

Terylene	benzene-1,4-dicarboxylic acid and ethane-1,2-diol	ester link
Nylon 6,6	1,6-diaminohexane and hexane-1,6-dicarboxylic acid	amide link
Kevlar	benzene-1,4-diamine and benzene-1,4-dicarboxylic acid	amide link

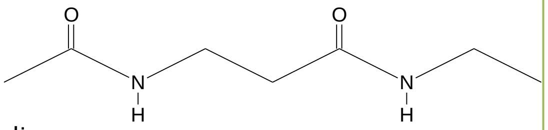
2. Intermolecular forces

Polyesters



Permanent dipole permanent dipole forces
The C is ∂^+ and the O is ∂^- so the molecule is polar

Polyamides



Hydrogen bonding
Dipole on NH and lone pair on oxygen

3. Comparison of addition and condensation

Polymers	Addition	Condensation
Monomer	Alkene	With 2 functional groups
Synthesis	No by product	H_2O
Repeating unit	Symmetrical	Asymmetrical
Reactivity	Non-polar so inert	Polar so undergo hydrolysis
Disposal	Some recyclable	Biodegradable

4. Disposal of polymers

Method	Advantages	Disadvantages
Landfill	Cheap, easy, ethane produced can be collected and used, material does not need sorting	Needs land that could be used for farming, leaks can contaminate water, we are producing so much waste landfill can't cope
Fuel	Generates electricity, avoids use of more crude oil; material does not need sorting	Toxic gases (usually acidic) are often released, carbon dioxide contributes to greenhouse effect, must be carefully controlled.
Recycling	Reduces plastic waste, reduces land fill, conserves fossil fuels, reduces energy use, reduces CO_2, NO, SO_2 emissions. Some are remoulded, some are cracked into monomers (chemical feedstock)	Difficult to do, collecting and sorting expensive, not all suitable plastic gets recycled, easy to contaminate, can't always use product to make what you started with.

5. Hydrolysis

Polyesters
Reflux with acid or alkali
Acid catalyst: carboxylic acid and alcohol
Alkali catalyst: carboxylate salt and alcohol

Polyamides
Reflux with acid or alkali
Acid catalyst: carboxylic acid and amine salt
Alkali catalyst: carboxylate salt and amine

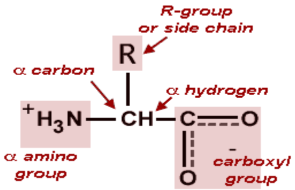
Unit 12a: Amino acids, proteins and enzymes

1. Keywords

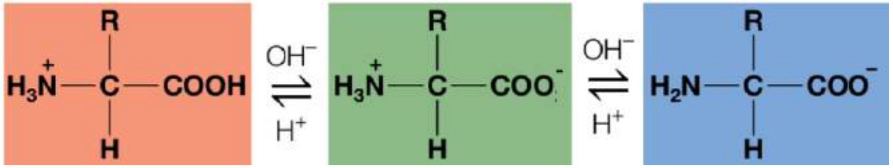
Denaturing	destroy the characteristic properties of an enzyme by heat, acidity, or other effect which disrupts its intermolecular forces
Peptide	a chain of amino acids joined by peptide links
Hydrogen bond	interaction between the negative dipole on a lone pair of electrons on a very electronegative atom and the positive dipole on a hydrogen bonded to a very electronegative atom.
Zwitterion	a neutral molecule with positively and negatively charged groups which cancel out

2. Structure

- Contain both amine (NH_2) and carboxyl (COOH) functional groups
- Chiral (not glycine)
- Exist as **zwitterions**
- Act both as acids and as bases
- α- amino acids have the amine group on the carbon next to the COOH group



Aminoacids with acids and bases



Proteins are sequences of amino acids joined by peptide links –CONH-

Proteins can have 4 structures:

- Primary structure: the sequence of amino acids within a repeat backbone of peptide bonds
- Secondary structure: Either an α-helix or a β-pleated sheet. Coiling and folding of a protein as a result of hydrogen bonding between peptide links
- Tertiary structure: The 3-D shape of a protein held together by hydrogen bonding, ionic interactions and sulphur-sulphur bonds between R groups
- Quaternary structure: arrangement of two or more folded polypeptide chains and metal ions

Sulfur-sulfur bonds.

- The amino acid cysteine has a side chain with a $-CH_2SH$ group.
- When oxidised, two cysteine molecules can form a sulfur-sulfur bond that makes a bridge between the two molecules; this is called a disulfide bridge.
- A double amino acid called cystine is formed.

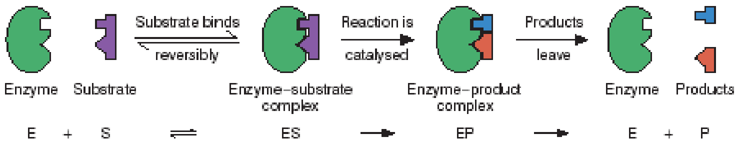
$$-CH_2SH + HSCH_2- + [O] \rightarrow -CH_2S-SCH_2- + H_2O$$

3. Hydrolysis

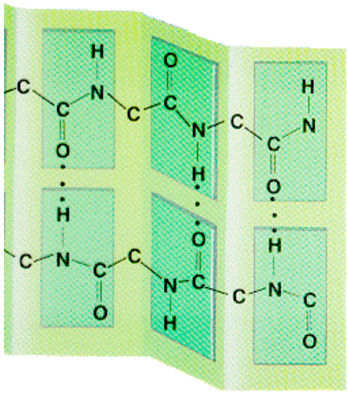
- Breaking down the primary structure of a protein or a peptide into its constituent amino acids
- Reflux for 24 hours with 6 mol dm^{-3} HCl
- Thin layer chromatography used to identify individual amino acids
- Spots colourless so develop with iodine/ninhydrin, view under UV
- Rf values- distance moved by spot ÷ distance moved by solvent
- Rf value depends on attractions between stationary and mobile phases

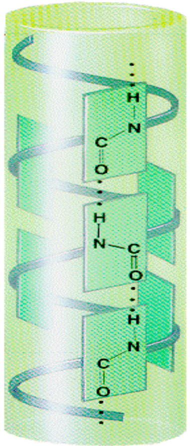
3. Enzymes

- Enzymes are biological catalysts
- **Stereospecificity:** The active site of an enzyme can be so specific that many enzymes will only catalyse reactions of one enantiomeric form of a substrate.



- Drugs can act as inhibitors by blocking the enzyme active site.
- Drug development by trial and error or computer modelling of best fit molecules



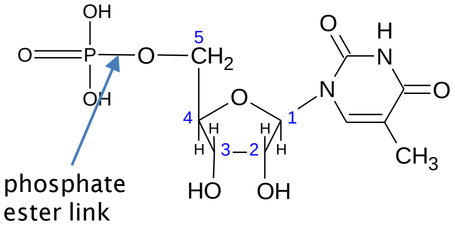


Unit 12b: DNA and cisplatin

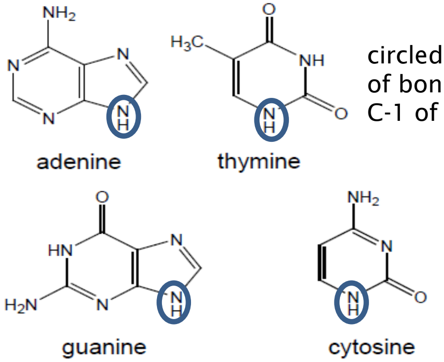
1. DNA

Deoxyribonucleic acid
Made of nucleotides

phosphate 2-deoxyribose base

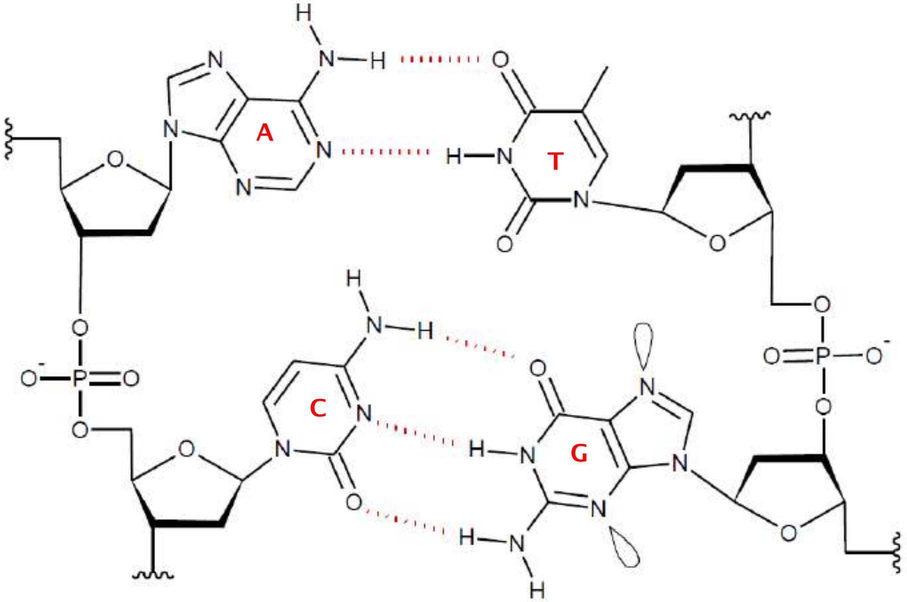


All bonds are formed by condensation



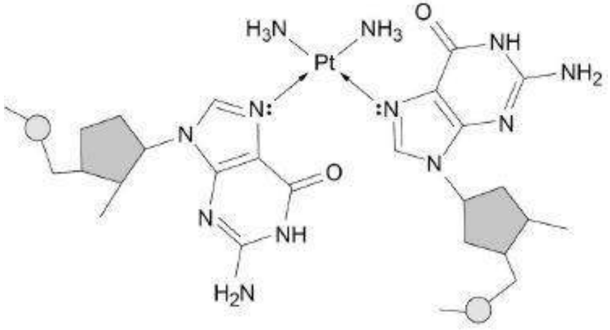
circled is point of bond with C-1 of sugar

A single strand of DNA is a polymer of nucleotides linked by covalent bonds between the phosphate group of one nucleotide and the 2-deoxyribose sugar of another nucleotide.
This results in a sugar-phosphate-sugar-phosphate polymer chain with bases attached to the sugars in the chain.
DNA exists as two complementary strands arranged in the form of a double helix.
The DNA Double helix is stabilised by hydrogen bonds between bases of complementary chain (A – T, C-G)



2. Anticancer drugs

- Cisplatin is an anticancer drug
- As it enters a cell, one of the chloride ligands is replaced by water to form a complex
  $[Pt(NH_3)_2Cl_2] + H_2O \rightarrow [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$
- Cisplatin prevents DNA replication in cancer cells by a ligand replacement with DNA where the water ligand bonded to platinum is replaced by a nitrogen atom in a guanine nucleotide and the Cl bonded to platinum is also replaced by a nitrogen atom in another guanine nucleotide.



Side effects:

- It will bond to DNA in healthy cells as well as cancerous ones.
- Must consider ethics of drug use

Unit: 14 Organic synthesis

1. Keywords

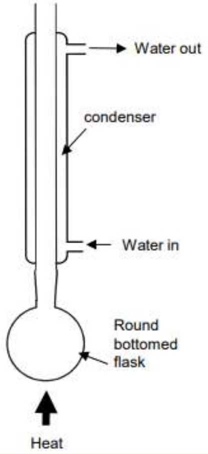
Atom economy:	a measure of the percentage of reactants that become useful products $\frac{M_r \text{ desired product}}{M_r \text{ of all reactants}} \times 100$
Target molecule:	desired product of a synthetic process.

2. Synthesis

Using organic reactions, you can work out a reaction scheme to convert a starting material into a **target molecule**.

- Start by writing down the formula of the starting molecule and the target molecule.
- Write down all the compounds which can be made from the starting molecule and all the ways that the target molecule can be made.
- Keep the number of steps as small as possible to reduce energy loss and increase yield
- Keep the atom economy high to reduce waste
- Chemists aim to design processes that do not require a solvent and use non-hazardous starting materials as this is more sustainable and has less environmental impact.

3. Reflux



Never seal the end of the condenser as the build up of gas pressure could cause the apparatus to explode.

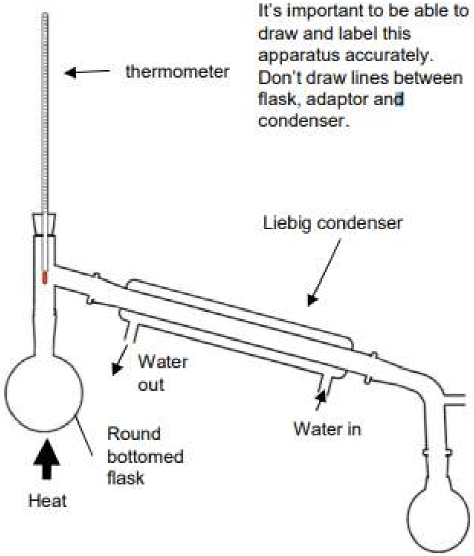
Anti-bumping granules are added to the flask in both distillation and reflux to prevent vigorous, uneven boiling

- 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

Electric heaters are often used to heat organic chemicals.

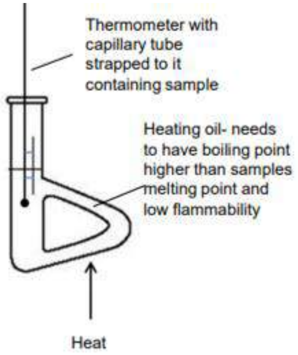
4. Distillation

- Used to separate an organic product from its reacting mixture.
- The distillate will be collected at the approximate boiling point range of the desired liquid.



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

5. Thiele tube



A Thiele tube is used to measure melting points.

- If impurities are present the melting point will be lowered and the sample will melt over a range of several degrees Celsius.
- The capillary tube is strapped to a thermometer immersed in some heating oil.
- Melting point can also be measured in an electronic melting point machine
- In both cases a small amount of the sample is put into a capillary tube.
- The tube is heated up and is heated slowly near the melting point

Unit 15: NMR

1. Nuclear Magnetic Resonance - theory

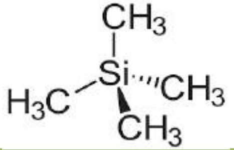
Scientists have developed a range of analytical techniques which together enable the structures of new compounds to be confirmed
Nuclear magnetic resonance (NMR) gives information about the position of 13C or 1H atoms in a molecule.
13C NMR gives simpler spectra than 1H NMR
Each atom of each compound will have its specific chemical shift (δ)
Chemical shift depends on the molecular environment.
Integrated spectra indicate the relative numbers of 1H atoms in different environments.

Solvents used

- $CDCl_3$ or CCl_4 solvent
- Both have no H atoms so give no signals in spectrum
- CCl_4 non-polar (good solvent for non-polar organic molecules)
- $CDCl_3$ polar covalent molecule (good solvent for polar organic compounds)

Reference

- TMS as reference
- Lots 12 equivalent H atoms give one signal
- Signal in an area away from other typical H signals
- Easy to remove / volatile / low bp

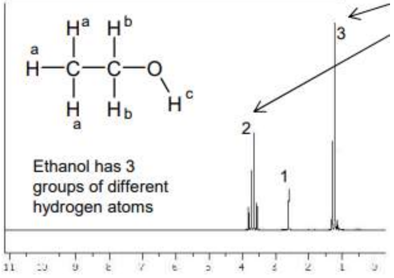


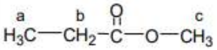
3. Interpretation of 1-H NMR

- The area of each peak is related to the number of H atoms producing it.
- The instrument produces a line called the integration trace. The relative heights of the steps show the relative number of each type of hydrogen.
- The peaks can be split into multiple smaller peaks (spin-spin coupling). These split into the number of hydrogen atoms on the adjacent carbon plus one. Following the n+1 rule.

Equivalent Hydrogen atoms.

In an H NMR spectrum, there is one signal for each set of equivalent H atoms.



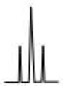
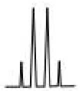


$$\overset{a}{H_3C}-\overset{b}{CH_2}-\overset{O}{\overset{\|}{C}}-O-\overset{c}{CH_3}$$

The peak due to group **a** will be a **triplet** as it is next to **b** (a carbon with 2 H's)

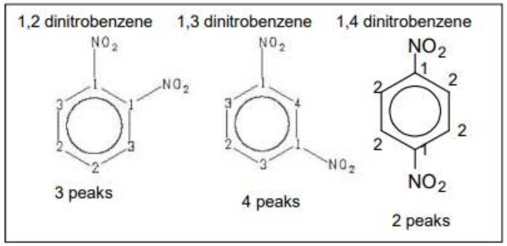
The peak due to group **b** will be a **quartet** as it is next to **a** (a carbon with 3H's)

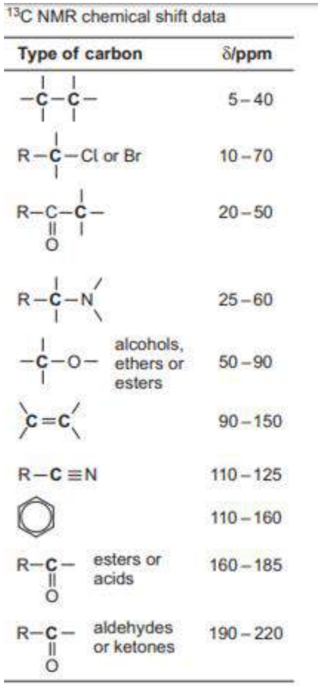
The peak due to group **c** will be a **singlet** as it is next to a carbon with no H's)

signal	singlet	doublet	triplet	quartet
appearance				
Split number of peaks	1	2	3	4
number of neighbouring inequivalent H atoms	0	1	2	3
relative size		1:1	1:2:1	1:3:3:1

2. Interpretation of 13-C NMR

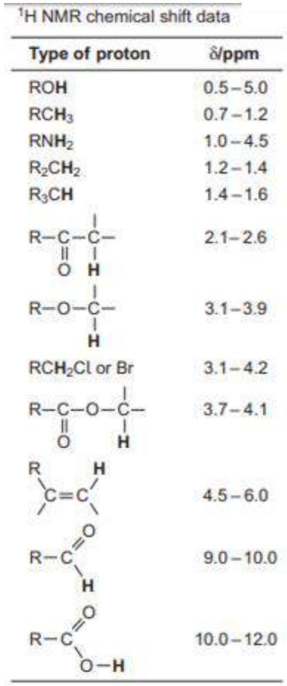
- Environment: If two carbon atoms have exactly the same sequence of bonds from them, they are in the same environment. Can be identified by looking at symmetry in molecules.
- Peak: Each carbon environment will have its own peak
- Shift: Value on scale given on data sheet





^{13}C NMR chemical shift data

Type of carbon		δ/ppm
$-C-C-$		5 – 40
$R-C-Cl$ or Br		10 – 70
$R-C(=O)-C-$		20 – 50
$R-C-N$		25 – 60
$-C-O-$	alcohols, ethers or esters	50 – 90
$C=C$		90 – 150
$R-C\equiv N$		110 – 125
benzene ring		110 – 160
$R-C(=O)-$	esters or acids	160 – 185
$R-C(=O)-$	aldehydes or ketones	190 – 220



^1H NMR chemical shift data

Type of proton	δ/ppm
ROH	0.5 – 5.0
RCH_3	0.7 – 1.2
RNH_2	1.0 – 4.5
R_2CH_2	1.2 – 1.4
R_3CH	1.4 – 1.6
$R-C(=O)-C(H)-$	2.1 – 2.6
$R-O-C(H)-$	3.1 – 3.9
RCH_2Cl or Br	3.1 – 4.2
$R-C(=O)-O-C(H)-$	3.7 – 4.1
$RC=CH$	4.5 – 6.0
$R-C(=O)H$	9.0 – 10.0
$R-C(=O)O-H$	10.0 – 12.0

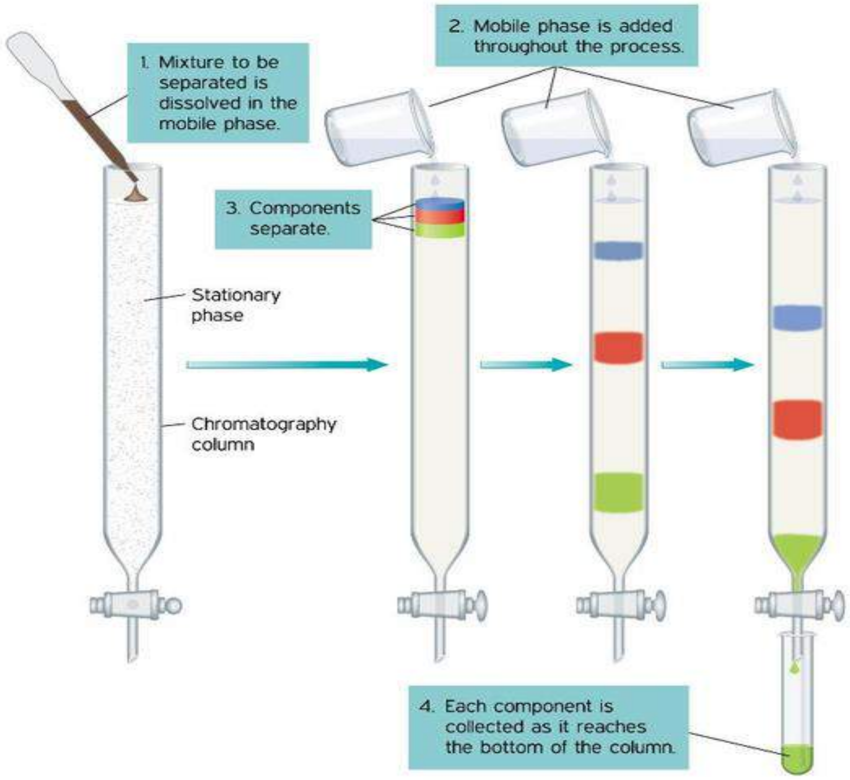
Unit 16: Chromatography

1. General principles

- Provides a method of separating and identifying components in a mixture
- Different types of chromatography are used depending on the composition of mixture to be separated
- Separation depends on the balance between solubility in the moving phase and retention by the stationary phase.
- Retention times and Rf values are used to identify different substances
- Compare retention times and Rf values with standards to identify different substances

3. Column chromatography (CC)

A column is packed with a solid and a solvent moves down the column
Allows individual components to be easily collected



2. Thin layer chromatography (TLC)

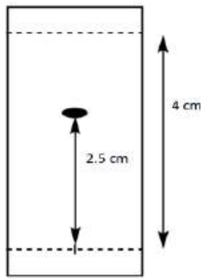
A plate is coated with a solid and a solvent moves up the plate
Advantages compared to paper chromatography:

- Faster
- Plates are harder wearing than paper
- Smaller amounts of mixtures can be separated

Detection

- Once a sample has run UV or developing agents such as ninhydrin or iodine are used to locate the spots
- The distance travelled relative to the solvent is called the R_f value

$$R_f = \frac{\text{distance travelled by the compound}}{\text{distance travelled by the solvent}}$$



$$R_f = \frac{2.5}{4} = 0.625$$

4. Gas chromatography (GC)

- A column is packed with a solid or with a solid coated by a liquid, and a gas is passed through the column under pressure at high temperature.
- The sample is carried by the gas and the mixture separates as some of the components move along with the gas and some are retained by the coated solid
- In GCMS (Gas Chromatography-Mass Spectrometry) a mass spectrometer is used as the detector and identifies the components produced