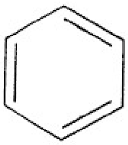
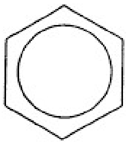
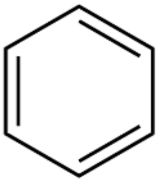
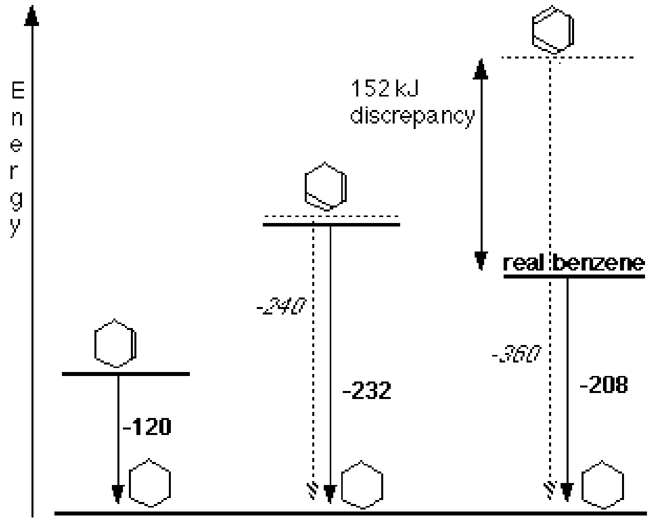
6.1.1 Aromatic compounds

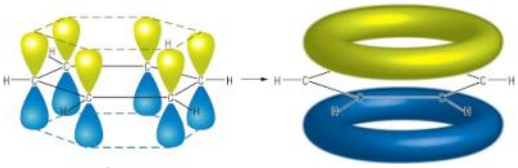
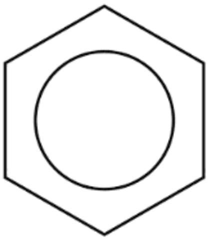
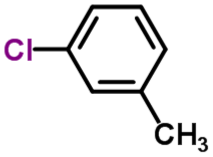
Definitions

Term	Definition
Arene	Aromatic compounds that contain a benzene ring as part of their structure

The benzene ring

- Benzene
  - An arene consisting of a ring of 6 carbon atoms each bonded to 1 hydrogen atom
  - Formula C_6H_6
  - Has a ring of delocalised electrons
  -  
- Benzene properties
  - Colourless, sweet smelling, flammable liquid
  - Found in crude oil/cigarette smoke
  - Is a carcinogen (causes cancer)
- The Kekulé model
  - 6 membered ring of carbon atoms joined by alternate single and double bonds
  - 
- Evidence to disprove the Kekulé model
  - Lack of reactivity of Benzene
    - Benzene is less reactive than alkenes
    - Bromination of benzene requires a catalyst/halogen carrier
    - It cannot have C=C bonds
  - Lengths of C-C bonds
    - All bonds were **the same length** measured using X-ray diffraction
    - Bond length is in **between length of single and double bond**
  - Hydrogenation enthalpies
    - Expected to be 3 times more exothermic than if there were 1 double bond only as there are 3 double bonds
    - Less exothermic than predicted

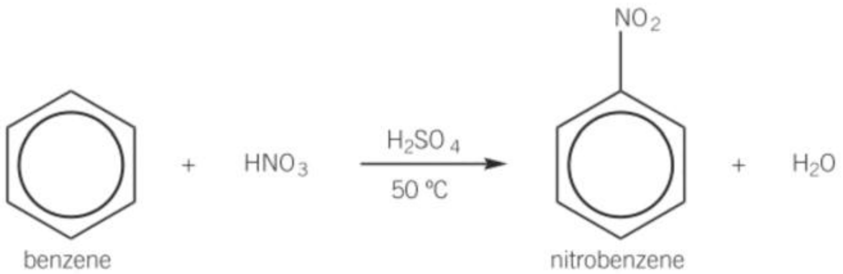
        - 

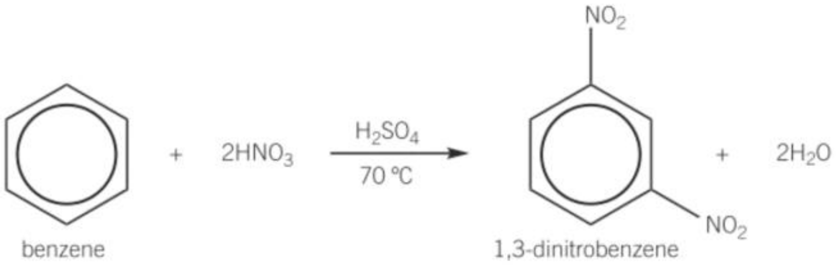
- The delocalised model
    - Benzene is a planar, cyclic, hexagonal hydrocarbon with 6 carbon atoms + 6 hydrogen atoms
    - Carbon uses 3 of its 4 electrons to bond to 2 other carbon atoms and 1 hydrogen atom
    - 1 electron left in p-orbital at right angles to plane of bonded carbon and hydrogen atoms
    - p-orbitals overlap sideways above + below plane of carbon atoms, forming a ring of electron density
    - Overlapping of p-orbitals creates a system of π-bonds, spreading across all 6 carbon atoms in ring
    - Electrons in π-bonds are delocalised
    - 
    - 
- Naming aromatic compounds
    - 1 substituent group = monosubstituted
        - Benzene ring = parent chain
            - Other chain = added as prefix to benzene
        - Benzene ring attached to an alkyl chain of 7 or more carbon atoms
            - Benzene = substituent
            - Prefix phenyl added to the alkyl chain with position
    - More than 1 substituent group
        - Decide the benzene + alkyl group based on
        - Groups listed as prefix
        - Ordered by alphabetical order
        - Numbered with lowest numbers possible (alkyl group = numbered as 1, not written in name)
        - e.g. 3-chloromethylbenzene
        - 

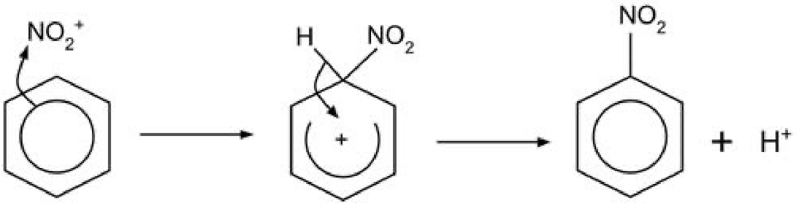
Electrophilic substitution reactions of benzene

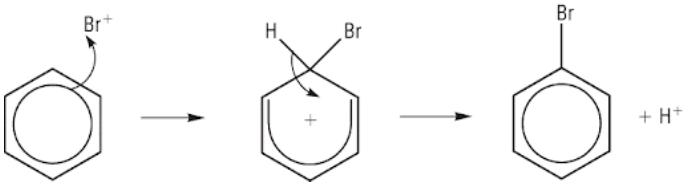
- Electrophilic substitution of benzene

  - A hydrogen atom on the benzene ring is replaced by another atom or group of atoms
  - 

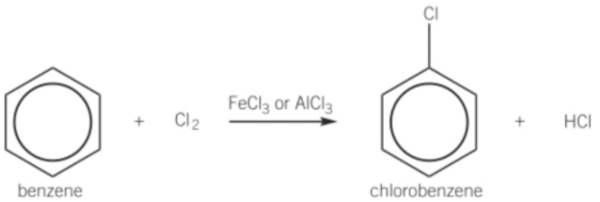
- Nitration of benzene
  - Temperature = 50°C
  - Catalyst = concentrated sulfuric acid
  - If temperature > 50°C further substitution may occur
  - 

  - 

- Mechanism for nitration of benzene
  - Formation of electrophile NO_2^+
    - $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$
  - Electrophilic addition
    - 

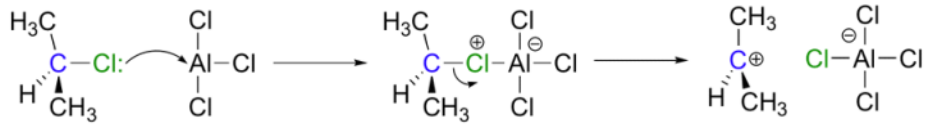
  - Regeneration of catalyst
    - $H^+ + HSO_4^- \rightarrow H_2SO_4$
- Halogenation of benzene
  - Need a halogen carrier catalyst
    - e.g. $AlCl_3$, $FeCl_3$, $AlBr_3$, $FeBr_3$
    - Benzene is too stable to react with a non-polar Br / Cl molecule
    - Need to create an electrophile with a halogen carrier e.g. $AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$
  - Formation of electrophile (Br^+ / Cl^+)
    - $Br_2 + FeBr_3 \rightarrow FeBr_4^- + Br^+$
  - Electrophilic addition
    - 

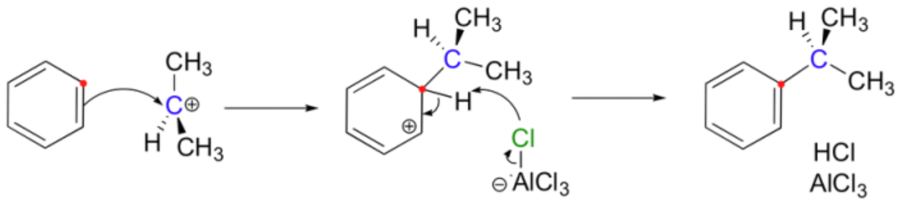
  - Regeneration of catalyst
    - $H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$
- Chlorination of benzene

- 

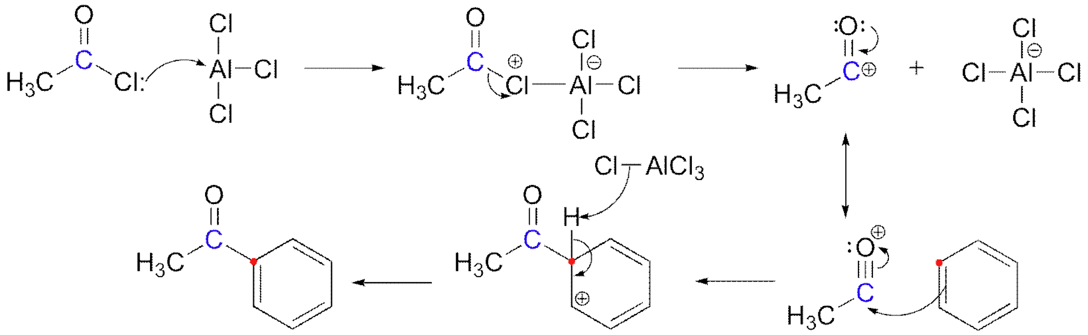
- Halogen carrier = $FeCl_3$ / $AlCl_3$
- Same mechanism as bromine

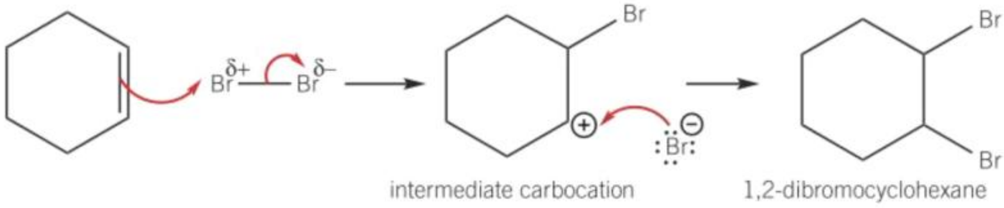
- Friedel-Crafts alkylation
  - Electrophilic substitution of a hydrogen atom by an alkyl group
  - React with haloalkane
  - Catalyst = $AlCl_3$
    - Acts as halogen carrier catalyst, generates the electrophile



- 

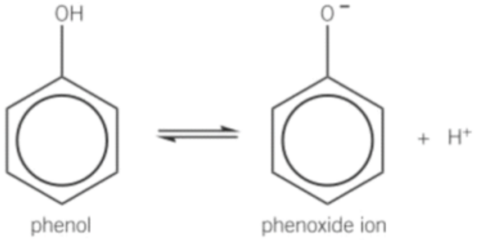
- Acylation reactions
  - Benzene reacts with an acyl chloride in the presence of an $AlCl_3$ catalyst by electrophilic substitution
  - Aromatic ketone formed



- Compare the reactivity of alkenes with arenes
  - Alkenes can react with Br_2 and decolourise bromine water
    - π-bond in alkene contains localised electrons above and below the plane of the 2 carbon atoms → area of high electron density
    - The π-bond electrons induces a dipole in non-polar bromine molecule (one is made slightly positive, the other slightly negative)
    - Slightly positive Br enables bromine molecule to act as an electrophile
    - 

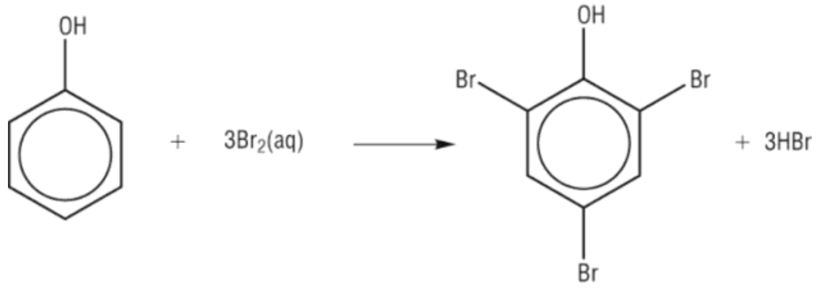
  - Benzene doesn't react unless a halogen carrier is present
    - It has delocalised π-electrons with less electron density around any 2 carbons than a C=C bond
    - Insufficient π-electron density around any 2 carbons to induce dipole in non-polar molecule, preventing a reaction taking place

Phenol

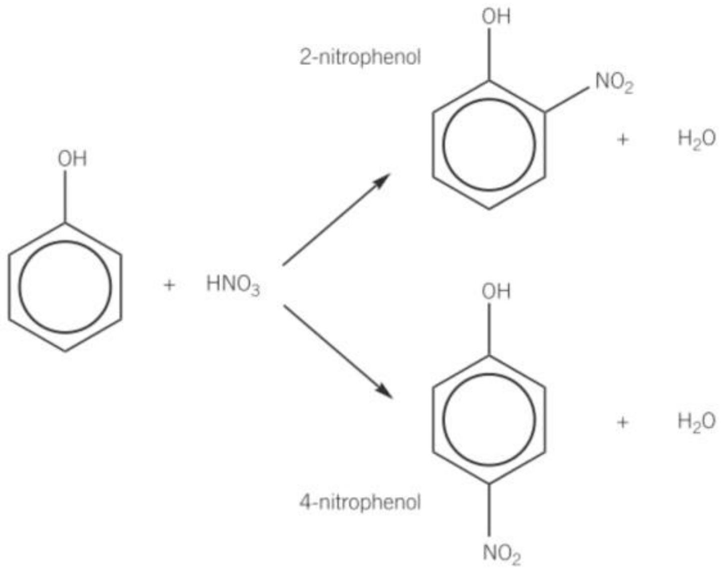
- Phenol
  - Contains a hydroxyl (-OH) group directly bonded to an aromatic ring
  - Simplest of phenols= phenol, C_6H_5OH
- Properties of phenol
  - Less soluble in water than alcohols due to non-polar benzene ring
  - Phenol = weak acid
  - When phenol dissolves it dissociates to phenoxide ion and a proton
  - Partially dissociates in aqueous solutions so classed as a weak acid
    - 

  - More acidic than alcohols but less acidic than carboxylic acids
    - K_a values: carboxylic acids > phenols > alcohols
    - pK_a values: alcohols < phenols < carboxylic acids
    -

Chemical	**Na**	**NaOH (strong base)**	**Na_2CO_3 (weak base)**
Ethanol	√	×	×
Phenols	√	√	×
Carboxylic acid	√	√	√

    - Test for whether carboxylic acid / phenol: react with Na_2CO_3, carboxylic acid will produce CO_2 (use lime water to test)
- Reactivity of phenols
  - The lone pair in the oxygen p-orbitals of the OH are donated to the delocalised π system in the ring
    - Increases the electron density in the delocalised π system
    - The ring is more negative and more susceptible to electrophilic attack
  - Comparisons
    - Bromine and nitric acid react more readily with phenol than benzene
    - Phenol nitrated with dilute nitric acid, benzene need concentrated nitric / sulfuric acid
- Bromination of phenol
  - React with an **aqueous solution of bromine** to form a **white precipitate** of **2,4,6-tribromophenol**
  - Reaction carried out at **room temperature and pressure**
  - Electron density in phenol can polarise Br_2 molecule so **no halogen carrier catalyst needed**
  - Decolourise bromine water from orange to colourless **immediately**
  - 

  - (3 bromines atoms are substituted into the ring, not 1)
- Nitration of phenol
  - Reacts with **dilute nitric acid at room temperature (no catalyst needed)**
  - A mixture of 2-nitrophenol and 4-nitrophenol is formed
  - Multiple substitution is possible but unlikely (after 1 nitro group is substituted into the compound becomes unreactive)

- 

Predicting substitution reactions

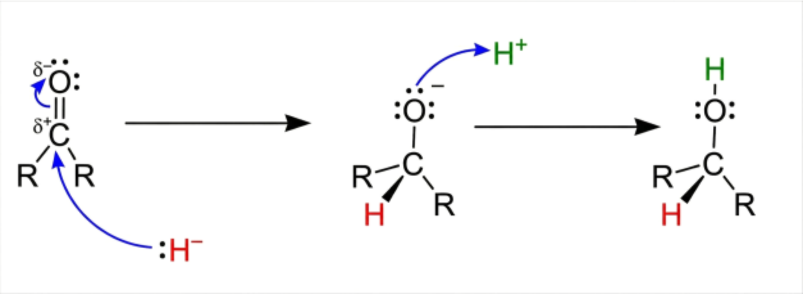
- Activating / deactivating groups
  - Activating
    - Donate electrons and **increase the π electron density** in the delocalised ring
    - Make the benzene ring more susceptible to electrophilic attack
    - Milder reaction conditions are needed (lower temperatures, more dilute acids, catalysts no longer needed)
    - Usually **2 and 4-directing** (e.g. **NH_2, OH, CH_3**)
  - Deactivating
    - Withdraw π electrons and **decrease the π electron density** in the delocalised ring
    - Make the benzene ring less susceptible to electrophilic attack
    - Stronger reaction conditions are needed (higher temperatures, more concentrated acids, catalysts)
    - Usually **3-directing** (e.g. **NO_2**, **COOH**)
    - Exception: Cl is deactivating and 2 and 4-directing
  - Exception: Cl groups deactivate the ring but is 2 and 4-directing
- Relative abundance of products
  - Position 2 = position 6 so about twice as much substituted at position 2 than position 4

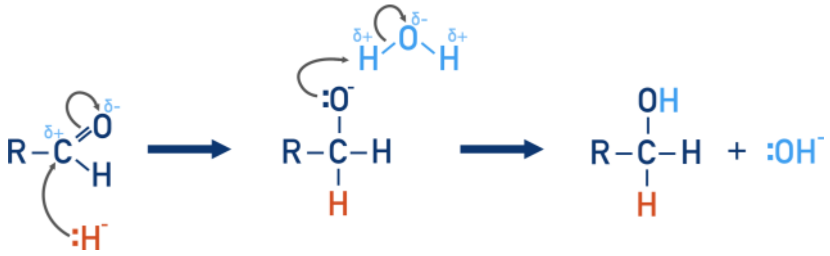
6.1.2 Carbonyl compounds

The carbonyl group

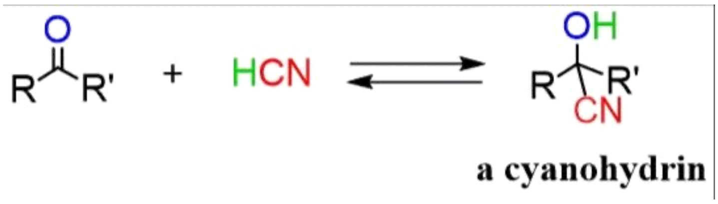
- Carbonyl functional group
  - C=O
- Naming carbonyl compounds
  - Carbonyl group on the end: structure is aldehyde, end with -al
  - Carbonyl group not on the end: structure is ketone, end with -one

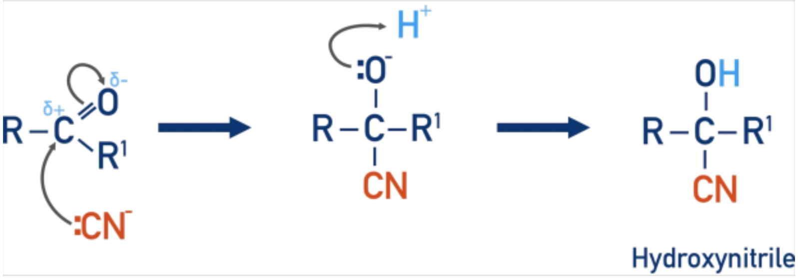
Reactions of carbonyl compounds

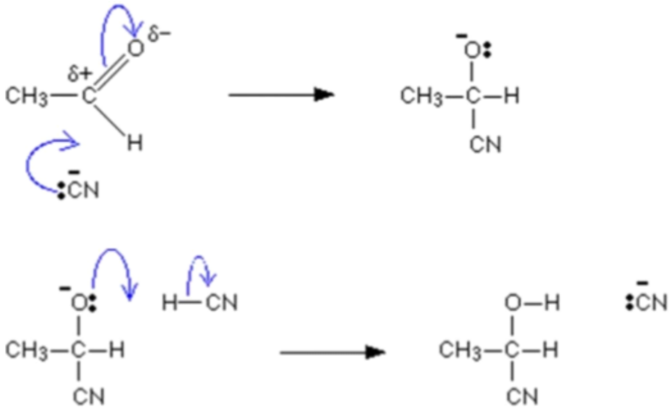
- Oxidation of carbonyl compounds
  - Aldehydes oxidised to carboxylic acids when refluxed with acidified dichromate (VI) ions ($Cr_2O_7^{2-}$ / H^+) e.g. acidified potassium dichromate
  - Ketones don't undergo oxidation
- C=O bond properties
  - Carbon-oxygen double bond is made up of a π-bond and a σ-bond
  - Same as C=C in alkenes, but C=C bond is nonpolar and C=O bond is polar
  - Oxygen is more electronegative than carbon so double bond lies closer to oxygen → carbon end slightly positive, oxygen end slightly negative
  - Polarity of C=O allows carbonyl compounds to react with nucleophiles (attracted to δ+ carbon), resulting in addition across the C=O bond → nucleophilic reaction
- Reaction of carbonyl compounds with $NaBH_4$ (sodium tetrahydridoborate)
  - $NaBH_4$ = strong reducing agent, reduce aldehyde to primary alcohols and ketones to secondary alcohols
  - Reaction usually carried out in **reflux** using **water or ethanol as solvent**
  - $LiAlH_4$ is another reducing agent option (not on spec but might appear)
- $NaBH_4$ reaction mechanism
  - 

  - 

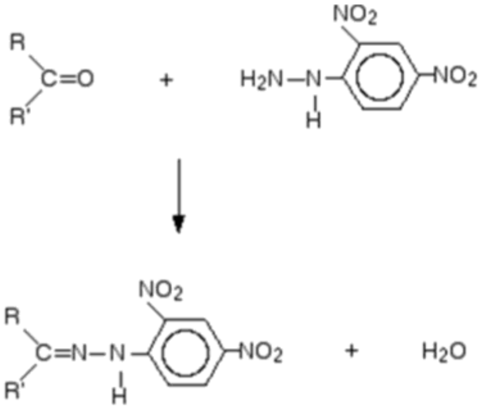
  - Reduction reaction / nucleophilic addition reaction
- Reaction of carbonyl compounds with HCN (hydrogen cyanide)
  - HCN adds across the C=O bond of aldehydes and ketones
  - HCN is colourless + extremely poisonous → too dangerous for open laboratory, sodium cyanide and sulfuric acid used to provide the hydrogen cyanide in the reaction
  - CN^- added to carbon atom
  - H^+ added to oxygen atom
  - **Increases the length of the carbon chain**

- 

- Mechanism for reaction with NaCN/H⁺
  - 

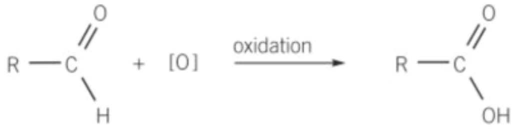
  - The H⁺ in the second step comes from **the water or acid** in the reaction mixture
- Alternative reaction mechanism with NaCN
  - 
  - CN^- in NaCN acts as a **catalyst** in the reaction
  - Almost all HCN (> 99%) will not ionise as it is a weak acid; NaCN ionises fully

Characteristic tests for carbonyl compounds

- Test for carbonyl group
  - Reagent = 2,4-DNP / 2,4-DNPH = 2,4-dinitrophenylhydrazine
  - React with the C=O group of an aldehyde / ketone to produce a **yellow precipitate** of a 2,4-dinitrophenylhydraz**one**
    - 
  - Identify the product from its melting point
    - Precipitate from 2,4-DNP test is filtered to separate solid ppt from solution
    - Solid is recrystallised to get pure sample
    - Melting point is measured & compared to database to identify compound
- Test for aldehyde using Tollen's reagent after carbonyl group is identified
  - Tollen's reagent is a very mild oxidising agent
    - It will oxidise aldehydes, but not ketones
  - Aldehydes will be oxidised to carboxylic acid and silver ions are reduced to silver metal
    - Aldehydes form a silver mirror, ketones do not

        - Inside of the reaction will be coated in silver metal if aldehyde is present
- Tollen's reagent reaction equation
    - Tollen's reagent is represented by [O] as it is an oxidising agent
    - $Ag^+(aq)$ ions act as an oxidising agent in the prescence of ammonia
    - Silver ions are reduced to silver as the aldehyde is oxidised to carboxylic acid

      $$Ag^+(aq) + e^- \xrightarrow{\text{reduction}} \underset{\text{sliver mirror}}{Ag(s)}$$

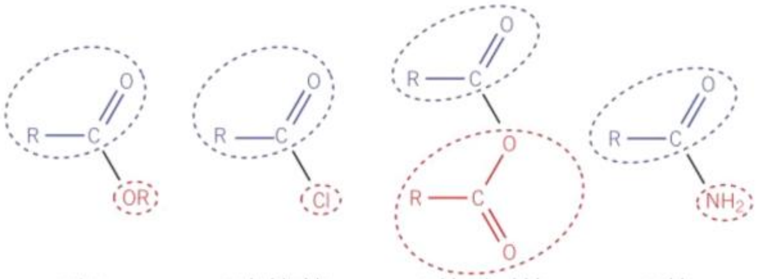
    - 

6.1.3 Carboxylic acids and esters

Definitions

Term	Definition
Esterification	A reaction in which a carboxylic acid reacts with an alcohol to form an ester and water

Nomenclature of carboxylic acids and esters

- Nomenclature
  - Carboxylic acid group: end in -oic acid
  - Carboxylate ion: end in -oate
- Carboxylic acid derivatives
  - 

    ester acyl chloride acid anhydride amide
  - Acyl group attached to an electronegative atom / group of atoms
- Naming ester
  - Named after the parent carboxylic acid from which it is derived (change -oic to -oate, add alkyl chain added to the COO group as the first word of the name)

Properties of carboxylic acids

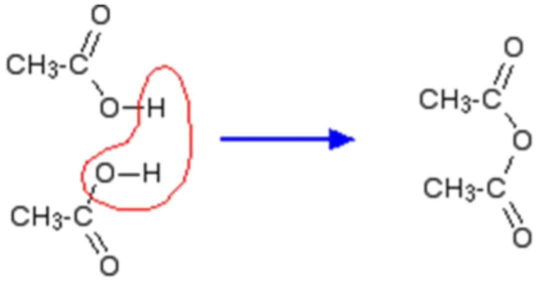
- Solubility of carboxylic acids
  - Carboxylic acids are **very soluble** in water
  - **C=O and O-H bonds are pola**r so they can form **hydrogen bonds** with water (explain what hydrogen bond is)
  - As the number of carbons increases, solubility decreases because non-polar carbon chain has a greater effect on overall molecule polarity (soluble for up to 4 carbon atoms)
  - Dicarboxylic acid = 2 polar carboxyl groups to form hydrogen bonds = dissolve readily in water + solid at room temp
- Acidity
  - Carboxylic acids are **weak acids**
  - They only **partially ionise** when in solution

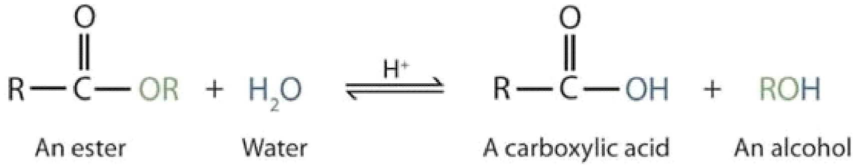
Reactions of carboxylic acids

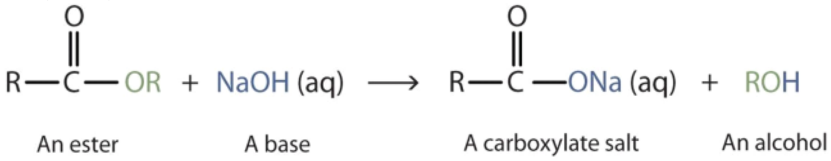
- With metals
  - Carboxylic acid + metal → salt + hydrogen
  - Slower than if the metal was reacted with a strong acid (fewer $H^+_{(aq)}$ ions at the same concentration)
- With bases
  - Carboxylic acid + metal → salt + water
  - Often very slow and usually need warming gently
- With carbonates
  - Carboxylic acid + metal → salt + water + carbon dioxide gas
  - Test for acid or carbonate (positive = effervescence)

Esters

- Esterification
  - 

  - Concentrated sulfuric acid catalyst
    - Speed up the reaction + absorbs the water produced and shifts equilibrium to RHS
  - The reaction mixture is warmed
- Acid anhydrides
  - Formed with 2 carboxylic acid molecules combine with the loss of water
  - 
- Ester formation with acid anhydrides
  - 

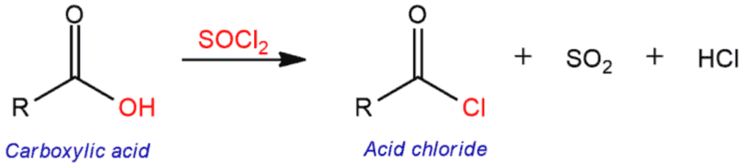
  - No catalyst required; require non-aqueous solvent + heating
  - Higher yield than using carboxylic acid itself
- Comparisons of acid anhydride esterification to other reactions
  - Acid anhydride is more reactive and more dangerous than the parent carboxylic acid
  - Acid anhydrides is less reactive than acyl chlorides so safer to use (also cheaper)
- Esterification of phenol
  - Phenol is not readily esterified by reacting it with a carboxylic acid
  - Phenol will undergo esterification with **an acid anhydride or an acyl chloride**
- Acid hydrolysis of esters
  - 

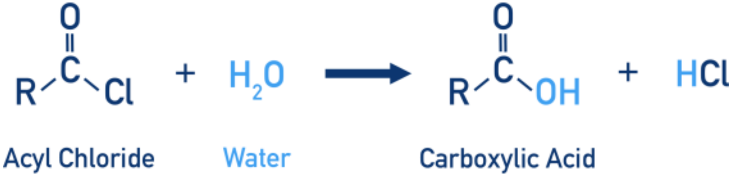
  - Heat under reflux with dilute aqueous acid
  - Ester broken down by water, acid = catalyst
  - (reverse of esterification)
- Alkaline hydrolysis
  - 

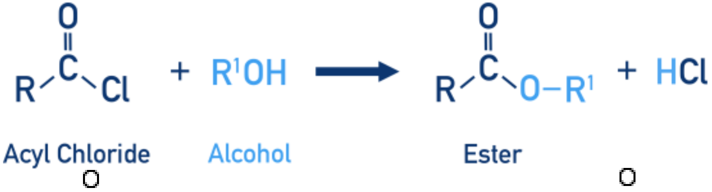
  - Heated under reflux with aqueous OH^- ions
  - Irreversible reaction

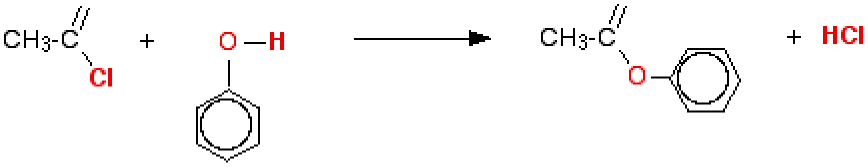
Acyl chlorides

- Acyl chlorides
  - When the -OH of the carboxylic acid is replaced with a -Cl group
- Formation of acyl chlorides (acylation)
  - React parent carboxylic acid + $SOCl_2$ (thionyl chloride)
  - Other products evolved as gases → only acyl chloride left
  - Reaction carried out in fume cupboard as the products are harmful

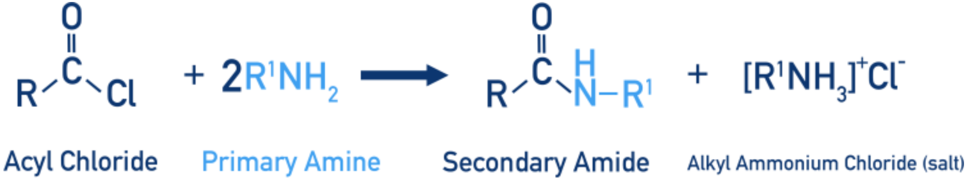
  - 

- Converting acyl chloride to carboxylic acid
  - Acyl chloride + water → carboxylic acid + HCl
  - 

- Acyl chloride to ester
  - Acyl chloride + alcohol / phenol → ester + HCl
  - 

  - 

- Amides formation
  - Acyl chloride + ammonia → amide + NH_4Cl
    - 

  - Acyl chloride + primary amine → secondary amide + alkyl ammonium chloride
    - 

* Notice that 2 ammonia / amine molecules are needed to balance the equation

6.2.1 Amines

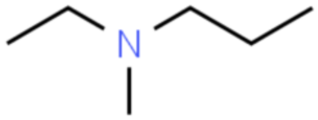
Definitions

Term	Definition
Amines	Substituted ammonia molecules that are produced when one or more hydrogen atoms in ammonia is replaced with an alkyl group

Nomenclature

- Classifying amines

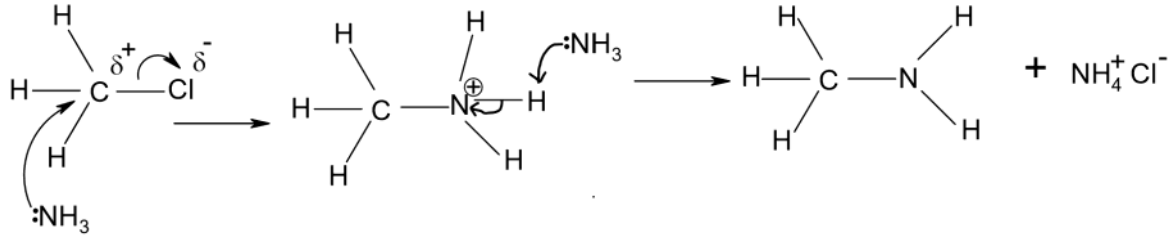
Number of hydrogen atoms substituted	Name
1	Primary
2	Secondary
3	Tertiary

- Naming primary amines
  - Use prefix amino- with a number to indicate the carbon atom that the nitrogen is attached to (e.g. 2-aminobutane)
  - If NH_2 is at end of the chain we can also add amine as suffix after name of the alkyl chain attached
- Naming secondary / tertiary amines
  - If they have the same alkyl group use di-/tri- to indicate number of groups on N (e.g.dimethylamine)
  - For different groups, it is an N-substituted derivative of the larger group (e.g. N-ethyl-N-methylpropylamine)
  - 

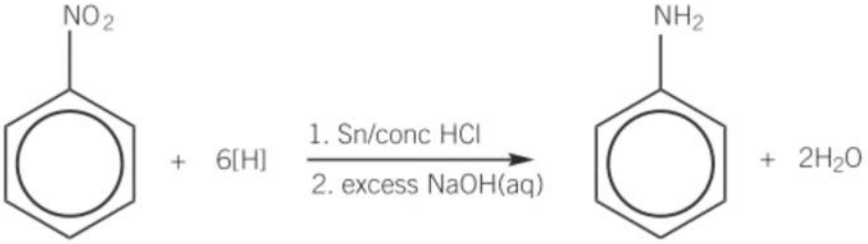
Basicity of amines

- Amines as bases
  - **Lone pair on the nitrogen** can accept a proton (base by Lewis acid definition)
  - Amines can **neutralise** acids to make salts
    - Amine + acid → quaternary ammonium salt
    - **No water is in the equation** (is produced but not written in equation)

Preparation of amines

- Formation of primary aliphatic amines
  - 

  - Prepared by **reacting haloalkanes with excess ethanolic ammonia**
  - Ethanol used as solvent → prevents any substitution of haloalkane by water to produce alcohols; haloalkane doesn't dissolve well in water
  - Excess ammonia used → reduces further substitution of amine group to form secondary / tertiary amines (use up haloalkanes as soon as possible)
- Formation of secondary and tertiary amines
  - Primary amine + haloalkane → secondary amine + salt of primary ammonium ion and chloride

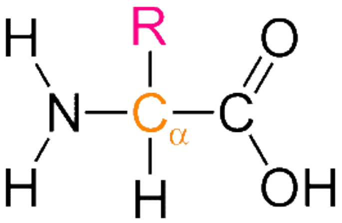
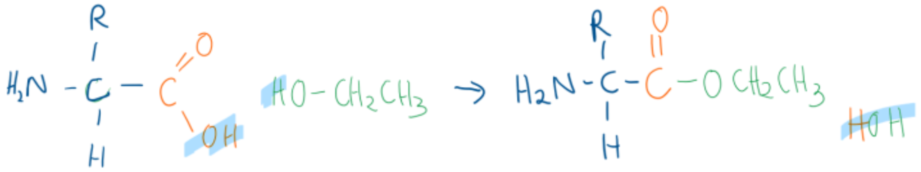
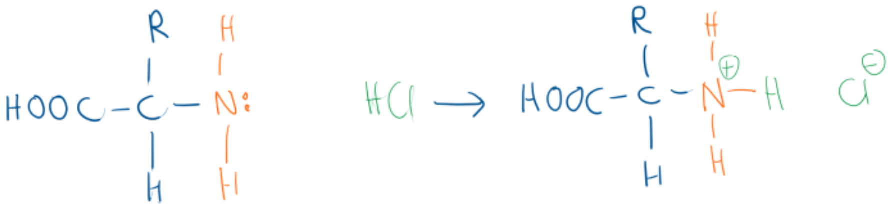
ion
    - Secondary amine + haloalkane → tertiary amine + salt of secondary ammonium ion and chloride ion
    - Mechanism same as formation of primary amine; swap both ammonia with primary / secondary amine
- Formation of aromatic amines
    - Made by reduction of **nitroarenes**
    - Heated under reflux with tin and concentrated HCl to form the ammonium salt
        - Tin + HCl = reducing agent
    - Ammonium salt reacted with excess NaOH to produce the aromatic amine
    - 

6.2.2 Amino acids, amides and chirality

Definitions

Term	Definition

Reactions of amino acids

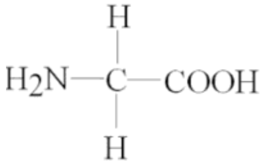
- Amino acids
  - An organic compound containing both amine (NH_2) and carboxylic acid ($COOH$) functional groups
  - General formula for α-amino acids: $RCH(NH_2)COOH$
    - ○ 
    - * The amine group and the -COOH group must be connected to the same carbon atom
- Reactions of the carboxylic acid group
  - React with aqueous alkali to form a salt + water
    - ○ 
  - Esterified by heating with an alcohol in the presence of concentrated sulfuric acid (+ water formed as side product)
    - ○ 
- Reaction of the amine group
  - The amine group is basic and can react with acids
  - React with acids to accept a proton (become fully protonated)
    - ○ 

Amides

- Amides
  - The products of reactions of acyl chlorides with ammonia and amines
  - Common in nature
  - Primary / secondary / tertiary: 1 / 2 / 3 carbon atoms bonded to N

Chirality

- Chiral centre

  - A carbon atom that is attached to **4 different atoms or group of atoms**
  - **Optical isomerism** is found in molecules with a chiral centre
  - * All amino acids except glycine contain a chiral carbon atom bonded to 4 separate groups
  - 

glycine

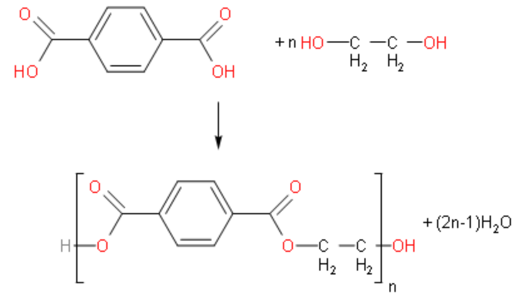
- Enantiomers
  - Two non-superimposable mirror image structures (optical isomers)
  - 2 per chiral centre

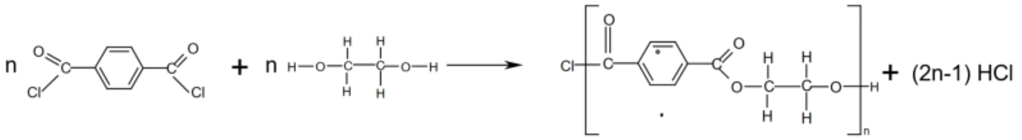
6.2.3 Polyesters and polyamides

Definitions

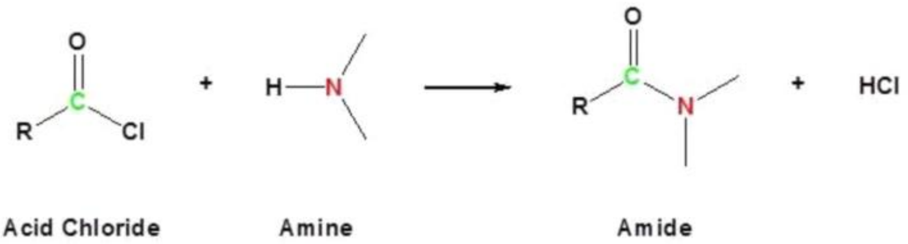
Term	Definition
Condensation polymerisation	The joining of two monomers with loss of a small molecule (usually water)
Polyamides	Condensation polymers formed when monomers are joined together by amide linkages in a long chain to form a polymer

Condensation polymerisation

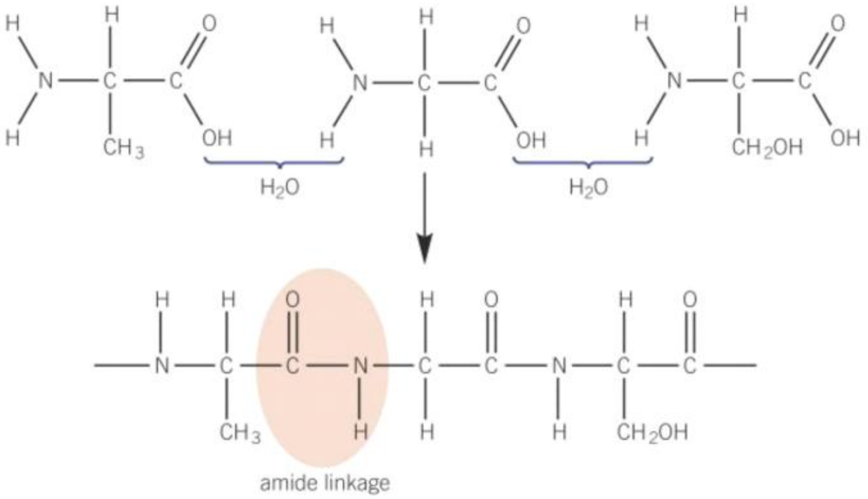
- Polyester formation by 1 monomer with 2 different functional groups
  - -OH + -COOH group
  - Carboxylic acid + alcohol group react together to form ester linkage + water
- Polyester formation by 2 monomers each with 2 functional groups
  - 1 diol (2 × -OH) + 1 dicarboxylic acid (2 × -COOH)
    - 

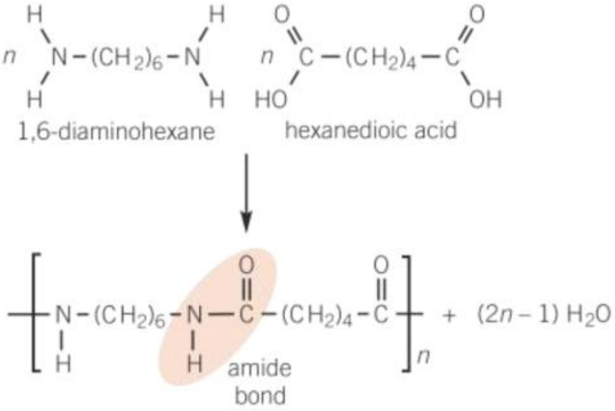
  - 1 diacyl chloride + 1 diol
    - 

  - Usually doesn't form through acid anhydrides
- Amides formation reactions
  - Carboxylic acid + amine → amide + H_2O
  - Acyl chloride + amine → amide + HCl

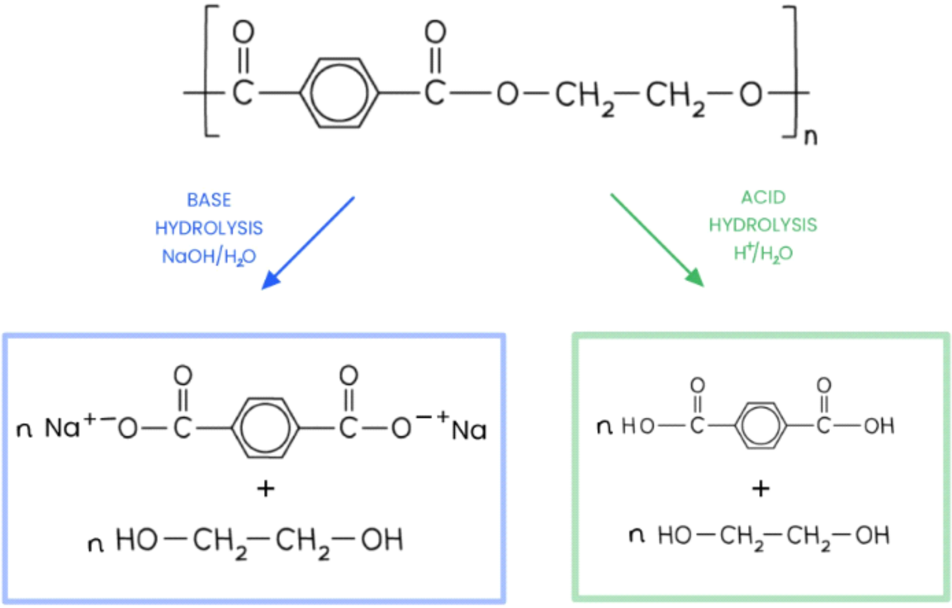
  - 

- Formation of polyamides by amino acids (1 monomer with 2 functional groups)
  - Amine group + carboxylic acid group
  - Amino acids undergo condensation polymerisation to form polypeptides (proteins)
  - Water lost when amide bond formed

- 

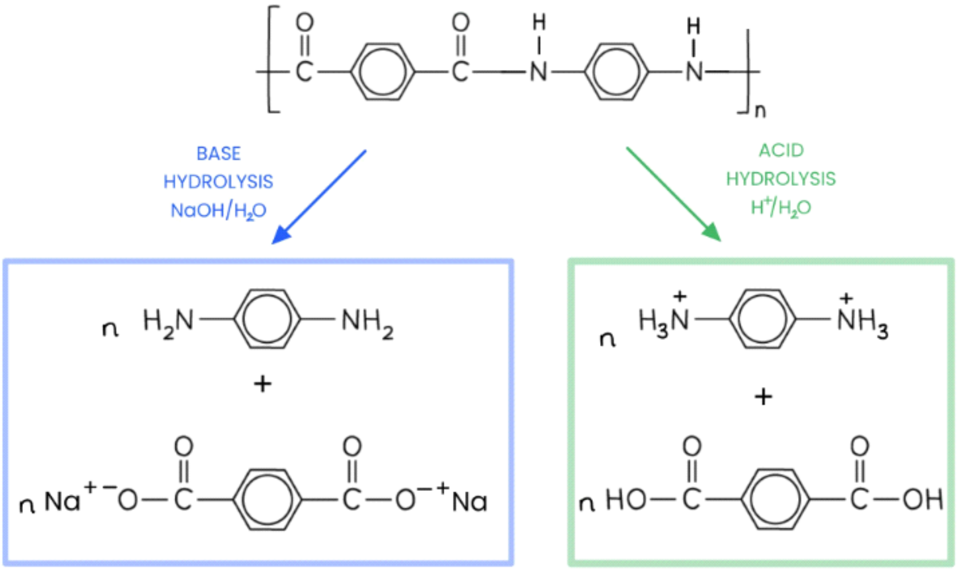
- Formation of polyamides by 2 monomers each with 2 functional groups
  - Dicarboxylic acid / diacyl chloride + diamine
  - Amide bond forms between the amine on 1 monomer + carboxyl / acyl chloride on the other monomer
  - 

Hydrolysis of polymers

- Hydrolysing polyesters
  - Acid hydrolysis forms the diol and dicarboxylic acid that were used to form the polyesters
  - Alkaline hydrolysis forms the diol and dicarboxylic acid salt
  - 

- Hydrolysing polyamides
  - Acidic hydrolysis
    - An acid (e.g. HCl) acts as the catalyst
    - Polyamides such as Kevlar are heated with dilute acid
    - This reaction breaks the polyamide into a dicarboxylic acid and ammonium ions

- Alkaline hydrolysis
    - The polyamide is heated with a species containing hydroxide ions (e.g. NaOH)
    - This breaks the polymer into the sodium salts of its monomers (dicarboxylic acid salt and diamines)

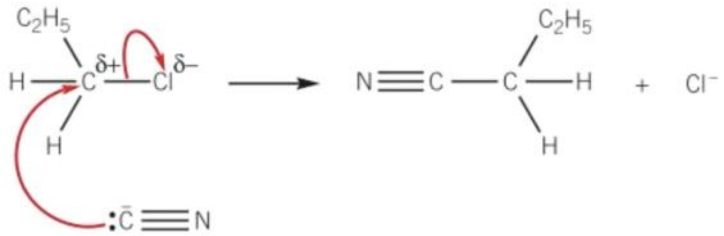
- 

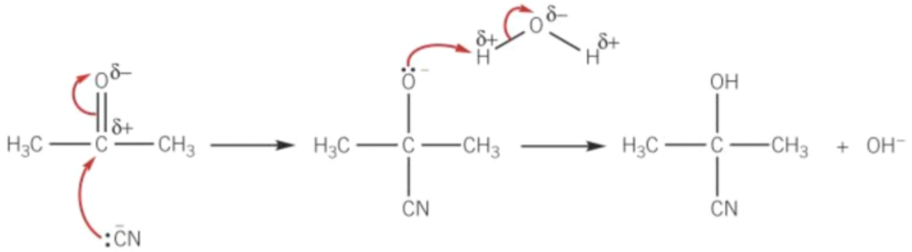
Predicting reactions

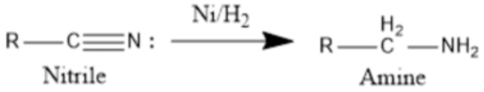
- Identifying monomers and repeat units
    - Addition polymerisation characteristics
        - C=C double bond in monomer
        - Backbone of polymer is a continuous chain of carbon atoms
    - Condensation polymerisation
        - Two monomers each with two functional groups / one monomer with two function groups
        - Polymer contains ester / amide linkages

6.2.4 Carbon-carbon bond formation

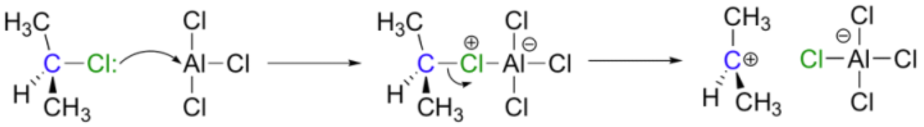
Extending carbon chain length

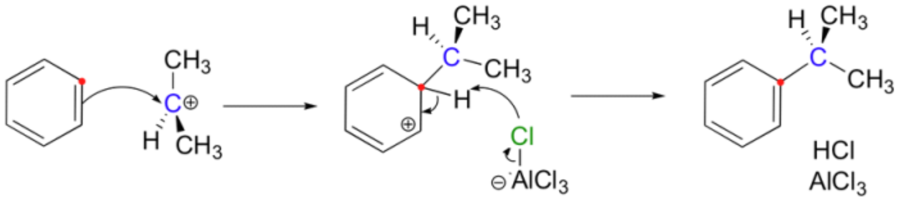
- Formation of nitriles from haloalkanes
  - **Heat haloalkanes under reflex with solution of NaCN or KCN in ethanol**
  - Nucleophilic substitution reaction
  - 

- Formation of nitriles from carbonyls
  - React aldehydes or ketones with HCN
  - A mixture of sodium cyanide + sulfuric acid can be used as hydrogen cyanide is too poisonous + this increases the rate of reaction
  - Nucleophilic addition reaction
  - Hydroxynitrile formed
  - 

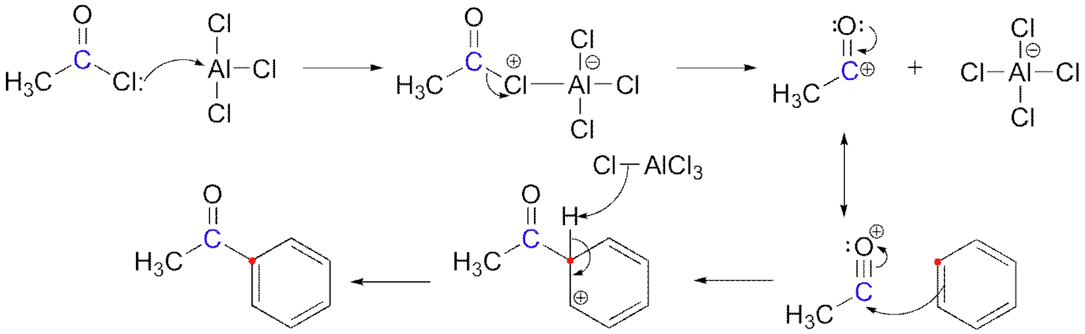
- Reduction of nitriles
  - Nitriles reduced to amines by reacting with hydrogen with nickel catalyst
  - Catalytic hydrogenation
  - 

- Alkylation / acylation of benzenes (also see 6.1.1)
  - Creates a C-C bond between the benzene ring and the substituted group
  - Alkylation mechanism



    ○ 

  - Acylation mechanism

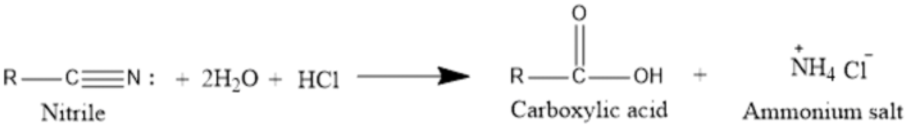


Reactions of nitriles

- Reduction of nitriles
    - Reduced to amines by **reacting with an reducing agent and adding Ni as catalyst**

-

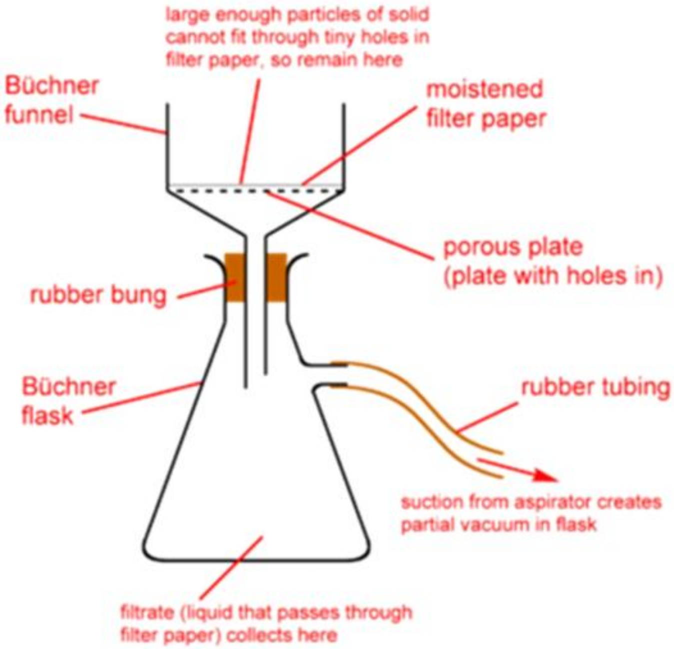
- Acid hydrolysis of nitriles
    - Form carboxylic acids by **heating with dilute aqueous acid e.g. HCl under reflux**

- 

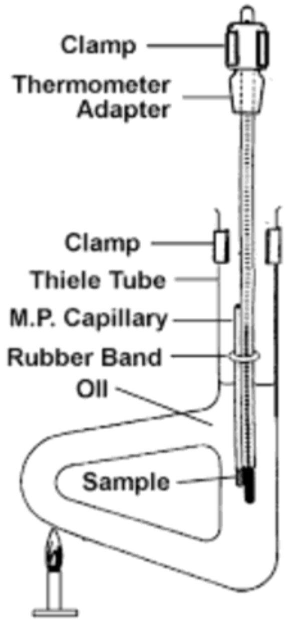
$R—C \equiv N: + 2H_2O + HCl \longrightarrow R—C(=O)—OH + \overset{+}{N}H_4 Cl^-$

6.2.5 Organic synthesis

Practical procedures

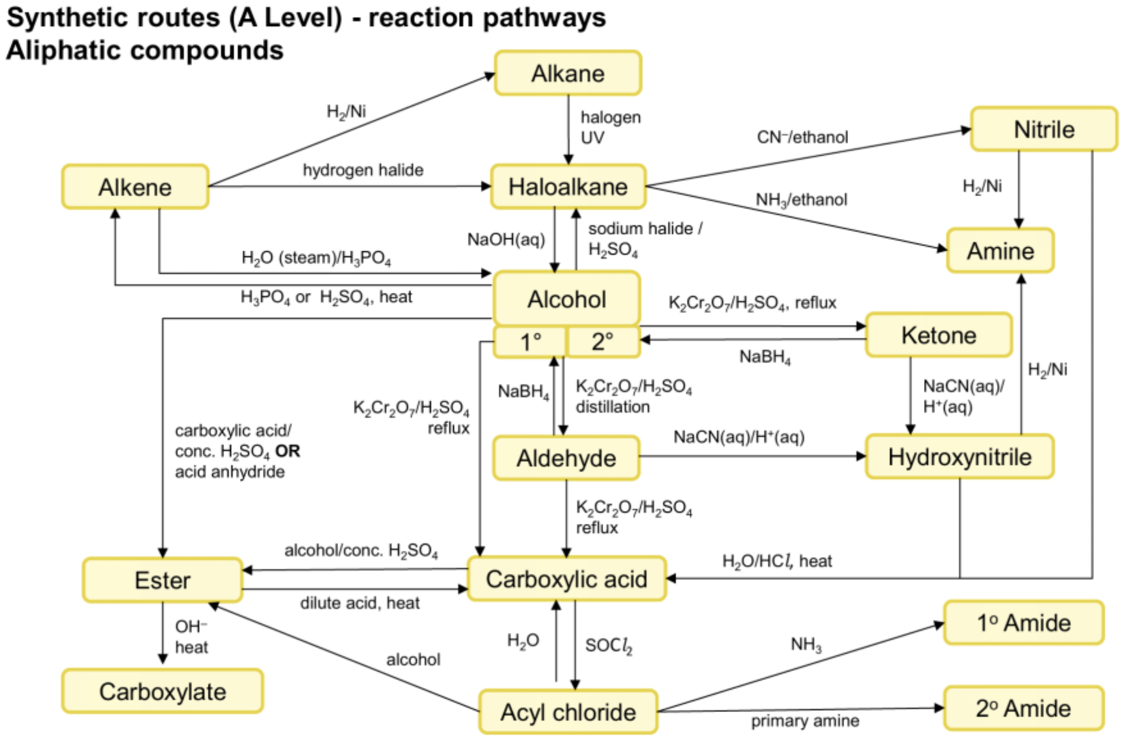
- Distillation with Quickfit apparatus
    - See 4.2.3
- Heating under reflux with Quickfit apparatus
    - See 4.2.3
- Methods to purify organic solid
    - Filtration under reduced pressure
    - Recrystallization
    - Measurement of melting points
- Filtration under reduced pressure
    - Use **the same solvent as in the mixture** to wet the filter paper / rinse beaker / rinse solid left over
    - 

- Recrystallisation
    - To remove impurities in solid after filtration
    - Impure solid is dissolved in the minimum amount of **hot solvent**
    - Pour chosen solvent into conical flask
    - The solution is cooled
    - The pure solid comes out of the solution as its solubility has been exceeded
    - The impurities and some of the pure substance will remain in the solution
- Verify purity with melting points
    - Find the melting range (difference in temperature between starting and finishing melting)
    - Pure sample: melting range should be 1/2° C
    - Impure sample: wider melting range, lower melting point than a pure sample (melting point depression)
- Measurement of melting points
    - Pack the substance into a capillary tube sealed at one end
    - Capillary tube then usually attached to a thermometer
    - Heat the tube in an oil bath in beaker / boiling tube
    - Record the temperature at which the solid started and finished melting (remove heat after melting started)
    - Alternative: heat the oil using a Thiele tube
        - This allows the oil to be heated more evenly

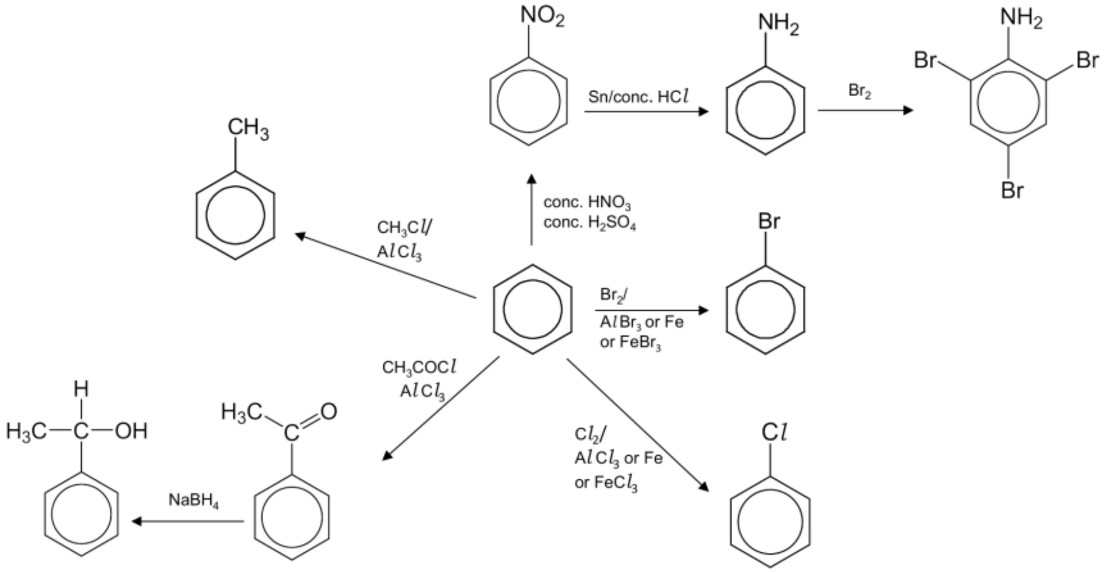


Synthetic routes

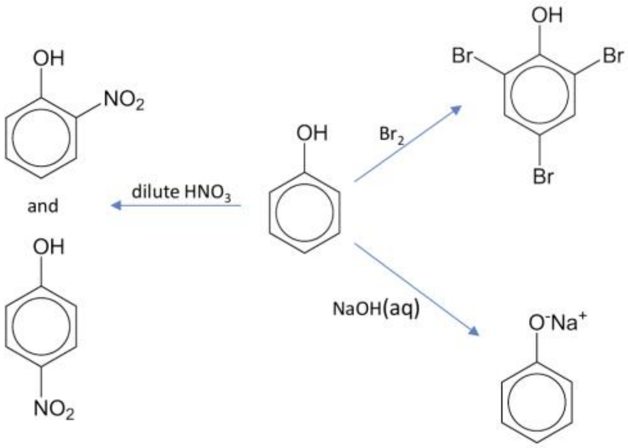
- Synthetic routes



Synthetic routes (A Level) - reaction pathways
Aromatic compounds

- 

Synthetic routes (A Level) - reaction pathways
Phenols

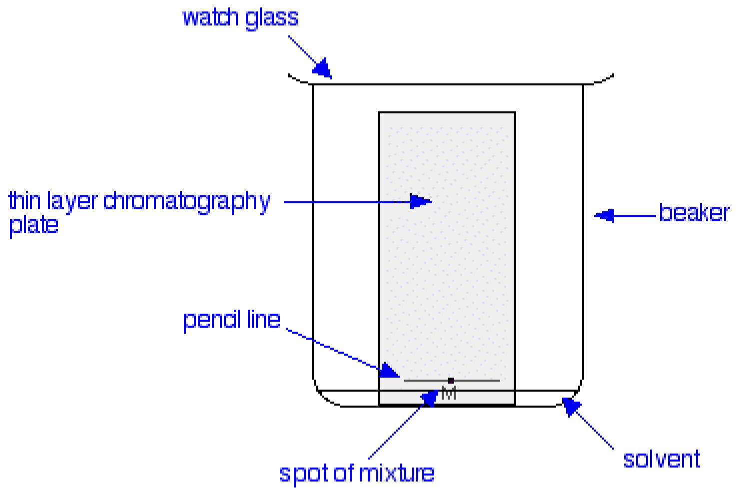
- 

6.3.1 Chromatography and qualitative analysis

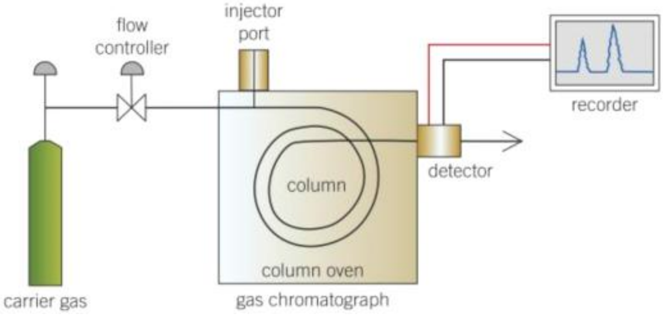
Definitions

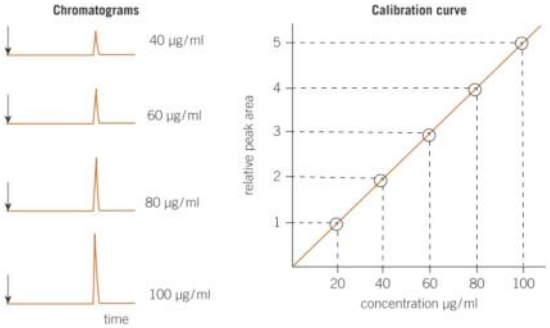
Term	Definition
Chromatography	Used to separate individual components from a mixture of substances
Adsorption	Process by which silica holds different substances in mixture to surface
Stationary phase	The phase that does not move in chromatography
Mobile Phase	The phase that moves in chromatography

Types of chromatography

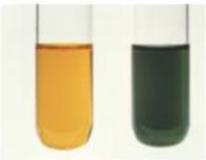
- Thin layer chromatography (TLC)
    - Mobile phase = the solvent in the tank moving up the TLC plate
    - Stationary phase = a thin layer of **adsorbent** e.g. SiO_2 or Al_2O_3 on a sheet or glass / plastic for support
    - Components separated by adsorption as they move at different rates
    - Different components have different affinities for adsorbent and bind with different strength to surface, meaning separation is achieved
    - Components identified by calculating retention factor ($R_f = \frac{\text{distance moved by component}}{\text{distance moved by solvent}}$)
    - 

- How to do a TLC
    1. Dissolve sample in a solvent
    2. Draw pencil line at bottom of plate
    3. Place spot of sample on line
    4. Plate placed into beaker and solvent added to below the line of the sample + lid
    5. When solvent comes near to the top, remove the plate and mark the solvent front in pencil
    6. Dry in oven
    7. Read the location of the spots
    8. Spots can be visualised with a locating agent: UV light / iodine vapour / Acidified potassium dichromate maganate (VII) dip (turns spots brown if they can be oxidised)
    9. Identify the substances present by calculating R_f values and compare to known data values / running TLC with known substances alongside
- Gas chromatography
    - To separate / identify volatile organic compounds
    - Stationary phase = a long tube possible with liquid coating inside
    - Mobile phase = inert carrier gas e.g. helium / neon
    - Small amount of mixture is injected into gas chromatograph and is carried by mobile gas through capillary column where it slows down as it interacts with liquid stationary phase
        - The components either adsorb onto the solid stationary phase or dissolve into a liquid stationary phase

        - i.e. separates by differences in relative solubility
    - The retention time for each sample is measured
        - Retention time = the time taken for a component to go from the inlet to the detector
        - Components that easily mix with the stationary phase emerge slower; those that are hard to mix emerge faster
        - Retention time can be compared to known values + peak integrations used to determine concentrations
    - The area under each peak is proportional to the amount of that component
        - Different substances of the same amount give different areas
    - 

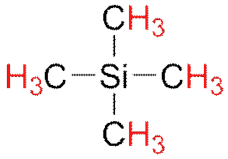
- Finding out concentration of a substance
    - Prepare standard solutions of known concentration
    - Obtain a gas chromatogram of the standard solutions
    - Plot a calibration curve of peak area vs. concentration
    - Obtain a gas chromatogram of compound being tested under the same conditions
    - Use calibration curve to obtain concentration
    - 

Tests for organic functional groups

Functional group	Chemical test	Observation	
alkene	add bromine water drop-wise	bromine water decolourised from orange to colourless	
haloalkane	add silver nitrate and ethanol and warm to 50 °C in a water bath	chloroalkane – white precipitate bromoalkane – cream precipitate iodoalkane – yellow precipitate	
carbonyl	add 2,4-dinitrophenylhydrazine	orange precipitate	
aldehyde	add Tollens' reagent and warm	silver mirror	
primary and secondary alcohol, and aldehyde	add acidified potassium dichromate(VI) and warm in a water bath	colour change from orange to green	
carboxylic acid	add aqueous sodium carbonate	effervescence	

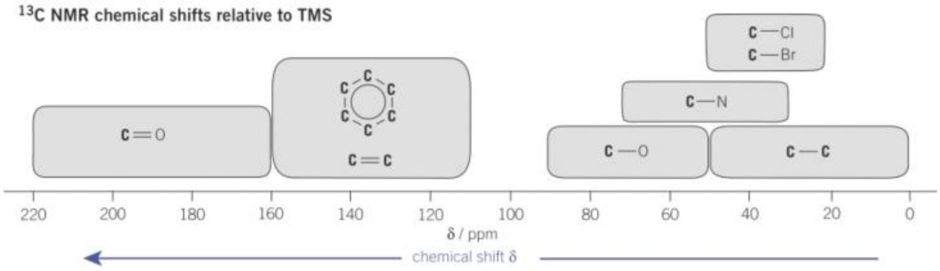
6.3.2 Spectroscopy

How does NMR work

- Frequency shift
    - Measured on a scale (chemical shift δ), units = parts per million (ppm)
- Standard chemical signal
    - TMS = the standard for chemical shift measurements
    - In TMS all ^{1}H and ^{13}C atoms are identical → only one peak
    - There is a large amount of each atom → very large peak
    - It is displaced a good distance from typical atoms → will not get it confused with the peaks caused sample
    - It is volatile → sample can be recovered
    - It is chemically unreactive
    - 

      tetramethylsilane (TMS)
- Why is deuterated solvent used
    - NMR only produces a signal when the atom has an odd number of particles in its nucleus
    - When ^{1}H is replaced by ^{2}H it produces no NMR signal
    - $CDCl_3$ is commonly used
        - It will produce peak in carbon-13 NMR but computers usually filter this out
        - It is volatile so the sample can be recovered

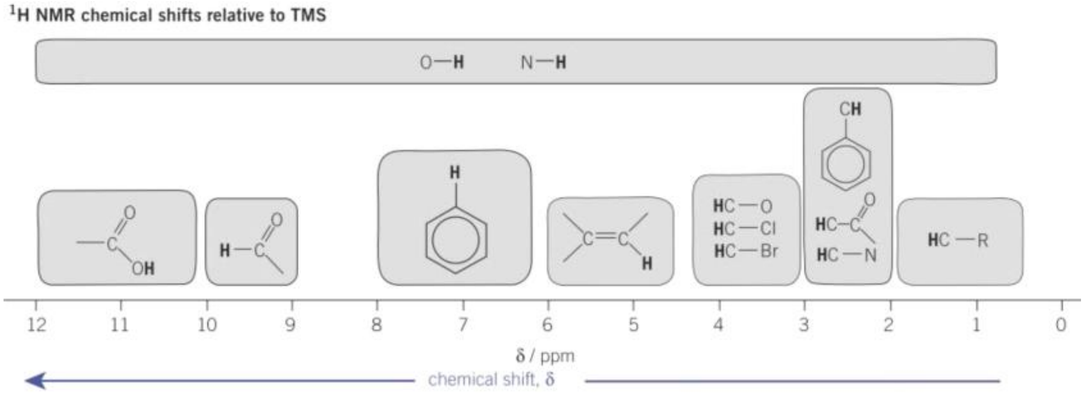
Carbon-13 NMR

- What carbon-13 NMR spectroscopy provides
    - Number of carbon environments (= the number of peaks)
        - Bonded to different atoms / groups of atoms = different environment + absorb at different chemical shifts
        - Two carbon atoms positioned symmetrically within a molecule are equivalent + have the same chemical environment→ contribute to same peak
        - Carbons nearer an oxygen atom will be shifted more to the left
    - Types of carbon environment (from the chemical shift)
        - 

- Work out molecule structure
    - State how many carbon environments there are
    - Link each shift value to its environment
    - Deduce overall structure based on those information
- Work out carbon-13 spectrum from the molecule structure
    - Work out all different environment + type
    - State the number of peaks within each chemical environment (__ peaks within __ to __ ppm)

Proton NMR

- What proton NMR spectroscopy provides
    - Number of proton environments (= number of peaks)

        - Protons at symmetrical positions = equivalent → absorb same shift → increasing peak size
        - Protons of different types = different chemical environments, non-equivalent → absorb different chemical shifts
    - Types of proton environments (from chemical shift)
        - 

    - Relative numbers each type proton (when using high resolution)
        - Area under each peak = integration area
        - Ratio of relative areas under each peak = ratio of protons responsible for each peak
        - Measured area under each peak as integration trace is shown as an extra line / printed number
    - Number of protons adjacent to given proton (due to spin-spin splitting)
        - For a proton with n protons on adjacent **carbon(s)** to the carbon that the proton is attached to, the number of sub-peaks is $n + 1$ (relative peak area worked out with Pascal's triangle)
        - Splitting pattern = singlet / doublet / triplet / quartet / quintet / hextet / septhet / multiplets
        - Hydrogens attached to nitrogen and oxygen **only show 1 sub-peak** and **doesn't increase the number of subpeaks of hydrogen attached to other adjacent carbon atoms**
- Proton exchange
    - Identifying -NH and -OH protons as they are often involved in hydrogen bonding so they can occur at almost any chemical shift + usually not involved in spin-spin coupling
    - NMR spectroscopy run as normal
    - Small volume of deuterium oxide (D_2O) is added, mixture is shaken
    - Deuterium replaces OH / NH protons with deuterium atoms
        - $R\text{-}O\text{-}H + D\text{-}O\text{-}D \rightleftharpoons R\text{-}O^- + H^+ + O\text{-}D^- + D^+$
        - $R\text{-}O^- + H^+ + O\text{-}D^- + D^+ \rightleftharpoons R\text{-}O\text{-}D + D\text{-}O\text{-}H$
        - Overall: $R\text{-}O\text{-}H + D\text{-}O\text{-}D \rightleftharpoons R\text{-}O\text{-}D + D\text{-}O\text{-}H$
    - NMR spectroscopy run again and the O-H and N-H peaks will disappear
        - Deuterium doesn't react to NMR spectroscopy as it has an even number of nucleons

Combined techniques

- What to infer from each information
    - Elemental analysis → empirical formula
    - Mass spectra → molecular mass
    - Infrared spectra → bonds and functional groups present
        - Identify the peak by absorption wavenumber
    - NMR spectra → carbon backbone and general structure
        - Identify the number of peaks and hence the number of non-equivalent protons
        - Identify the environment of each peak by its chemical shift on the delta scale
        - For proton NMR: use splitting pattern to identify what is on adjacent carbon atoms
    - Check with the mass spectrum to see if the masses of the fragment ions match