# 6.1 - Aromatic compounds, carbonyls and acids

## 6.1.1 - Aromatic compounds

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| **What was wrong with Kekule’s benzene structure and why?** | * Lack of reactivity…   + If it had 3 C=C bonds it’s expected to react rapidly with Br2 by electrophilic addition.   + It doesn’t react readily as its e- is too low - requires a catalyst and does so by electrophilic substitution. * Bond lengths…   + C=C bonds are shorter than C-C bonds ∴ benzene should be irregular/deformed.   + When bond length were measured. They were all the same, **intermediate in length** between single and double carbon-carbon bonds ∴ **regular** hexagonal shape. * Enthalpy change of hydrogenation…   + Scientists measured it to be -120kJmol-1 for cyclohexene ∴ with benzene we’d expect -360kJmol-1.   + Was measured to be -208kJmol-1 ∴ more stable than expected. |
| **Describe the π-ring in benzene and its consequences** | * Sideways overlap of 6 p-orbitals (containing 1 electron each) ∴ electron density above and below the plane spread over 6 carbons ∴ low electron density ∴ unable to polarise many molecules ∴ reactions require catalysts. * Delocalised electrons ∴ not attached to a single atom. |
| **Describe the nomenclature for polysubstituted arenes** | * The lowest number is given to the lowest position of the alphabet:     1-bromo-4-chloro-2-ethylbenzene   * When benzene is attached to an alkyl group with 7 or more carbons **OR** an alkyl with a functional group on it, it is the substituent:     *Phenylethanone*    *2-phenylhexane* |
| **Give the 3 non-systematic arenes you need to know** | *Benzoic acid*    *Phenylamine*    *Benzaldehyde* |
| **What are the conditions, reactants, steps (with mechanism), and precautions of nitration?** | * Conditions/reactants: 50 °C, conc. HNO3 (nitric acid), conc. H2SO4 (sulfuric acid).  1. Form the nitronium ion…    1. **Stage 1:** H2SO4 + HNO3 → HSO4- + H2NO3+    2. **Stage 2:** H2NO3+ → NO2+ + H2O    3. **Overall:** HNO3 + 2H2SO4 → NO2+ + 2HSO4- + H2O 2. React nitronium ion with benzene…       *The catalyst H2SO4 has reformed.*   * Perform within a water bath ∵ reaction is exothermic. Any temperature too high will lead to polynitration rather than mononitration |
| **What are the reactants and steps (with mechanism) of the halogenation of benzene?** | * Reactants: halogen carrier (e.g., FeBr3/AlBr3 for bromination and FeCl3/AlCl3 for chlorination) as a catalyst.  1. The halogen carrier polarises the halogen allowing it to react with the halogen carrier to form a positive electrophile.    * Br2 + FeBr3 → Br+ + FeBr4- 2. React the electrophile with the benzene…       *A positive electrophile has to be formed because benzene isn’t very polarising.* |
| **What are the conditions, reactants, and mechanism for Friedel–Crafts alkylation of benzene?** | * Conditions: heating under reflux. * Reactants: haloalkane with its halogen carrier (e.g., AlCl3 for CH3Cl). * Mechanism: electrophilic substitution,       The CH3Cl + AlCl3 forms [CH3]+ + [AlCl4]-. |
| **What is an acyl halide?** | Where R is an alkyl group and X is a halogen. |
| **What are the conditions, reactants, equation, and mechanism for Friedel–Crafts acylation of benzene?** | * Conditions: heating under reflux, 50 °C. * Reactants: acyl halide and halogen carrier (e.g., CH3COCl for AlCl3). * Equation: CH3COCl + AlCl3 →[CH3CO]+ + [AlCl4]-. * Mechanism: electrophilic substitution, |
| **How does benzene compare to other alkenes? (3)** | |  |  | | --- | --- | | **Benzene** | **Other Alkenes** | | Reacts by electrophilic substitution. | Reacts by electrophilic addition. | | 6 delocalised electrons in π-ring. 12 σ electrons localised between carbon atoms. | 2 localised electrons in π-bond. 2 localised electrons between σ-bond. | | Requires a catalyst (e.g., halogen carrier) to react ∵ electron density to low to polarise halogens due to delocalisation. | Reacts readily ∵ high electron density can induce dipoles on nearby halogens | |
| **How does the reactivity of methylbenzene and benzene compare?** | Methylbenzene is more reactive ∵ the side group releases electrons into the delocalised system ∴ increasing its electron density and thus reactivity.  *This is a positive inductive effect.* |
| **What is phenol?** | A benzene group with a -OH directly attached. |
| **What type of acid is phenol and how does it react with metals and bases?** | * A weak acid. * Reacts with metals and strong bases (e.g., NaOH) **YET** too weak to react with a weak base (e.g., NaCO3) (unlike carboxylic acids). |
| **How do alcohols react with bases?** | They don’t because they’re not acidic. |
| **How can you distinguish between phenol and a carboxylic acid?** | Carboxylic acids will react with a weak base (e.g., NaCO3) leading to effervescence **HOWEVER** phenol will not. |
| **How does phenol react with metals and bases?** | Forms a normal salt. |
| **Describe the bromination of phenol (product, conditions, reactants)** | * Forms a white ppt (can be used to distinguish from alkene as the bromine decolourises). * No halogen carrier required, reacts **readily**, room temperature. |
| **Describe the nitration of phenol** | Reacts readily with **dilute** nitric acid to form a mixture **OR** conc. nitric acid to produce 2,4,6-trinitrophenol. |
| **Why is phenol more reactive than benzene?** | As the lone pair p-orbital e-’s on the oxygen **partially delocalise** into the π-ring increasing its electron density so it can polarize (induce dipoles making molecules polar). |
| **Give 2 uses of phenol** | * Antiseptic (used by Lister, called carbolic acid). * Detergents. * Dyes. |
| **Describe the 3 cases with ‘directing groups’ with examples** | 1. **Unsubstituted ring** - electron density constant so electrophiles are equally likely to react with any carbon. 2. **Substituted with electron-donating group** (-OH or -NH2) - e-’s partially delocalise into the ring increasing its density at carbon 2, 4, 6 making them more likely to react. 3. **Substituted with electron-withdrawing group** (-NO2) - no e-’s to delocalise, withdraws density from the ring, particularly carbons 2, 4, 6 making 3, 5 more likely to react.   You can remember -NO2 as being an electron-withdrawing group since NO for "NOT OPEN". |

## 6.1.2 - Carbonyl compounds

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| **What are carbonyl compounds?** | An aldehyde or ketone (containing C=O bond). |
| **Are carbonyls soluble and if so, why and which ones?** | * Yes as it forms hydrogen bonds. * The small ones. |
| **How is Tollens’ Reagent formed? (aka ammoniacal silver nitrate)** | 1. By mixing NaOH (aq) to AgNO3 (aq) until a brown ppt is formed. 2. Adding dilute ammonia drop-by-drop until the ppt re-dissolves. |
| **How is Tollens’ Reagent formed and used? (aka ammoniacal silver nitrate)** | Aldehydes are oxidised by Tollens’ into carboxylic acids with Ag+ ions being reduced and coating inside of the test tube with a silver mirror, Ag+ (aq) + e- → Ag (s).    *It cannot happen with ketones as they cannot be oxidised.* |
| **How is Brady’s Reagent used to identify carbonyls? And how does it react? (3)** | * Reacts with carbonyls to form a white ppt (1)   (2)   * The melting point of the crystal formed can be used the carbonyl used (with the help of a database) (3) |
| **How are carbonyls reduced to alcohols? (without catalyst method) (reagents, conditions, mechanism, example equation)** | * NaBH4 is used as a source of hydride (H-) ions. * In ethanol solution. * Mechanism:      * Examples:   + CH3CH2CHO + 2[H] → CH3CH2CH2OH   + CH3COCH3 + 2[H] → CH3CH(OH)CH3   *[H] just means some reducing agent.* |
| **How are carbonyls reduced to alcohols? (with catalyst method) (reagents, conditions, example)** | * Reduced using catalytic hydrogenation. * Reagents: H2 and nickel catalyst. * Conditions: high pressure. * Examples: CH3CHO + H2 → CH3CH2OH |
| **What are nitriles?** | An organic compound that has a C≡N functional group |
| **How are nitriles named?** | The C≡N becomes part of the main chain (e.g., 2-hydroxy-2-methylpropanenitrile). |

## 6.1.3 - Carboxylic acids and esters

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| **How are carboxylic acids stablised?** | By delocalisation of e-’s making dissociation into a carboxylate ion more likely.    *The bonds are drawn the same as they’re actually identical.* |
| **How does the strength of carboxylic acids vary with carbon chain length and why?** | * Increasing length means weaker acid. * Increasing the length pushes e- density onto the COO- making it more negative thus less stable and less likely to form.   *Since the carbon is not very electronegative and cannot* |
| **How does chloroethanoic acid differ from ethanoic acid and why?** | * It’s more acidic. * The electronegative Cl withdraws e- density from the COO- ion making it less negative and more stable. |
| **What are salts of carboxylic acids called?** | Carboxylates. E.g, (CH3COO-)Na+ is called sodium ethanoate. |
| **What is different about methanoic acid to other carboxylic acids?** | It can be oxidised as its structure as it has an aldehyde group. |
| **How are esters named?** | The alcohol ends in -yl and is the prefix. The carboxylic acid ends in -anoate and is the suffix.    *This is called methyl-ethanoate.* |
| **What is esterification and how do you do it?** | Reacting carboxylic acids with alcohol to form esters. |
| **Describe the 2 types of esterification** | 1. Esterification using acid catalyst:    * Carboxylic acid + alcohol ⇌ ester + water    * Sulfuric acid catalyst required for H+ ions    * Heat under reflux 2. Esterification using acid anhydrides:    * Acid anhydride + alcohol → ester    * Room temperature    * Higher yield achieved |
| **What is an acid anhydride and how are they named?** | Two different carboxylic acids joined together. It is named alphabetically if the acids are different. E.g.,    *Ethanoic anhydride*    *Ethanoic methanoic anhydride* |
| **Give 2 ways esters can be hydrolysed** | 1. Heating with hot (aq) acid:    * Use sulfuric acid catalyst under reflux.    * Forms the original reactants.    * CH3CH2CO2CH2CH3 + H2O ⇌ CH3CH2COOH + CH3CH2OH (reversible so doesn’t give a good yield) 2. Heating with hot (aq) alkali (saponification):    * Use sodium hydroxide under reflux.    * Forms a carboxylate and alcohol.    * CH3CH2CO2CH3 + NaOH → (CH3CH2CO2- )Na+ + CH3OH   *The anion in the salt is resistant to attack by weak nucleophiles such as the alcohol so this reaction isn’t reversible.* |
| **How and why are acyl chlorides better than carboxylic acids?** | They are more reactive than carboxylic acids as Cl is a good leaving group. |
| **How are acyl chlorides formed?** | * By reacting carboxylic acid using SOCl2 (thionyl chloride). * CH3COOH + SOCl2 → CH3COCl + SO2 + HCl |
| **How do acyl chlorides react with water?** | To produce a carboxylic acid. |
| **How do acyl chlorides react with alcohols and why is it good?** | * To produce an ester. * It’s faster (∵ more reactive) and not reversible. |
| **How do acyl chlorides react with ammonia?** | To produce a primary amide. |
| **How do acyl chlorides react with primary and secondary amines? (with example equation)** | * To produce secondary and tertiary amides respectively. * Example:     *The N means that the methyl group is bonded to the nitrogen rather than the main carbon chain.* |
| **How do acyl chlorides react with phenol and why is this used?** | * Form an ester. * Phenol doesn’t react readily with carboxylic acids. |
| **What 2 things are common for most reactions of acyl chlorides?** | 1. Carried out at room temperature. 2. Any HCl (g) is given off at steamy white fumes |

# 6.2 - Nitrogen compounds, polymers and synthesis

## 6.2.1 - Amines

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| **What is an amine?** | A compound containing -NH2 group.    *This is dimethylamine.* |
| **How do you name amines if the substituent groups aren’t the same?** | As an N-substituted derivative of the longest carbon chain. Eg, N-ethylpropylamine: |
| **What do amines primarily react as?** | Bases. Eg, they react with HCl to produce methylammonium chloride (a salt)    This equation doesn't include the Cl- ion |
| **How are primary aliphatic amines formed? (with reactants, conditions, and equations)** | * Reactants: haloalkane and ammonia. * Conditions: excess ammonia (to prevent further substitution maximising no. of primary amines) and ethanol as solvent (preventing hydrolysis of haloalkanes). * Equations: |
| **How are secondary and tertiary aliphatic amines formed? (with reactants, conditions, and equations)** | * Reactants: haloalkane and primary / secondary amine. * Conditions: ethanol as solvent (preventing hydrolysis of haloalkanes). * Equations: |
| **How are aromatic amines formed from nitrobenzene? (conditions, reactants, type of reaction, and equation)** | * Conditions: reflux. * Reactants: Sn, conc. HCl and excess NaOH (required for hydroxide ions). * Type of reaction: reduction. |

## 6.2.2 - Amino acids, amides and chirality

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| **What are amides?** | A compound containing a -CONH2 group. |
| **How are primary amides formed? What precauation must be taken?** | * By reacting acyl chlorides with ammonia.      * You require a lot of NH3 to react with HCl to allow the reaction to go to completion. |
| **How are secondary/tertiary amides formed?** | By reacting acyl chlorides with a primary amine. Eg, |
| **What are amino acids?** | A central carbon with an amino group and carboxyl group. |
| **How are amino acids named?** | (2-)aminoethanoic acid |
| **What are optical isomers and what is required of them?** | * Stereoisomers that are non-superimposable mirror images. * 4 different groups attached to a carbon (called the chiral centre).     There are enantiomers / optical isomers.  *They can be distinguished by shining plane-polarised light and seeing the angle of rotation.* |
| **How can you look for the chiral centre on a cyclic molecule?** | Going around the ring in 2 directions and seeing if you encounter molecules the same way **OR** trying to draw a line of symmetry. If not either then they are enantiomers. |

## 6.2.3 - Polyesters and polyamides

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| **What are the 2 types of polymerisation?** | 1. Addition polymerisation. 2. Condensation polymerisation. |
| **What is addition polymerisation?** | When unsaturated monomers react. |
| **Why are poly(alkenes) non-biodegradable?** | They are chemically inert due to the **STRONG** and **NONPOLAR** C-C and C-H bonds. |
| **What is condensation polymerisation?** | Two different monomers that add together with a small molecule usually given off as a side-product (eg, H2O or HCl).  *These monomers usually have the same functional group on both ends of the molecule (eg, diamine, dicarboxylic acid, dioil, diacyl chloride).* |
| **Give the 2 most common types of condensation polymers with their linkage** | 1. Poly(esters) which contain an ester link (-COO-). 2. Poly(amides) which contain an amide link (-CONH-).   They form what is called an ester linkage or amide linkage. |
| **How and why are polyester and polyamides biodegradable?** | * They can be broken down by hydrolysis. * Due their polar nature attracting attacking species. |
| **Why may condensation polymers be photodegradable?** | As the C=O bond absorbs radiation. |
| **What are condensation polymers hydrolysed by? In what is each hydrolysed more easily?** | * Hot (aq) acid or alkali. * Poly(**a**mides) are hydrolysed more easily with strong **a**cid. * Poly(esters) are hydrolysed more easily with strong bases.     *It can be hydrolysed by water but it’s FAR too slow.* |
| **What does the base and acid hydrolysis of poly(esters) yield?** | 1. Base - dicarboxylate salt and diol. 2. Acid - dicarboxylic acid and diol. |
| **What does the base and acid hydrolysis of poly(amides) yield?** | 1. Base - dicarboxylate salt and diamine. 2. Acid - dicarboxylic acid and diammonium. |

## 6.2.4 - Carbon–carbon bond formation

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| **What are the reagents, conditions, mechanism for converting a haloalkane to nitrile?** | * Regant: :CN- (from NaCN / KCN) * Conditions: heating under reflux, dissolved in ethanol (since water will form alcohols) * Mechanism: nucleophilic substitution, |
| **What are the reagents, conditions, mechanism for converting a carbonyl to hydroxynitrile?** | * Regents: :CN- (from NaCN / KCN dissolved in ethanol since water will form alcohols) and dilute sulfuric acid. * Conditions: RTP. * Mechanism: nucleophilic addition.     H+ ion is supplied by H2SO4.  *HCN could be used yet it is a toxic gas and is difficult to gain.* |
| **What are the possible reagents and type of reaction for converting nitriles to amines? (with example)** | * Reagents: LiAlH4 **OR** H2 with Ni catalyst. * Type: reduction. * Examples:       *This particular example uses a different catalyst.* |
| **What are the reagents, conditions, type of reaction, and examples for converting (hydroxy-)nitriles to carboxylic acids?** | * Reagents: dilute acid (eg, dilute HCl). * Conditions: heating under reflux. * Type: hydrolysis. * Examples: |

## 6.2.5 - Organic synthesis

*You can learn the synthesis routes by learning the other flashcards.*

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| *Covered distillation and reflux.* | |
| **How can you purify an organic solid by recrystallisation? Why is each step used?** | 1. Pour the distillate of impure product into a separating funnel. 2. Wash with:    * NaHCO3 solution, shaking, releasing pressure from CO2 produced **TO NEUTRALISE ANY ACID IMPURITIES**.    * Saturated NaCl solution to seperate layers. 3. Allows layers to separate and discard aqueous layer (the organic layer will be on top usually, lower density). 4. Run organic layer into clean dry conical flask. 5. Add drying agent (eg, anhydrous sodium sulphate or calcium chloride) to dry liquid. When dry, it should be clear. 6. Decant liquid into flask and then distill to collect pure product.   *Decant means carefully pour off organic liquid leaving the drying agent in the conical flask.* |
| **What should you ensure with the drying agent for purifying organic liquids?** | * Be insoluble in the organic liquid. * Not react with the organic liquid. |
| **How can you purify an organic solid by recrystallisation? Why is each step used?** | 1. Dissolve impure compound in minimum volume of hot solvent.    1. To ensure saturated solution. 2. Filter using filter paper quickly.    1. Removing any insoluble impurities. 3. Cool filtered solution by inserting beaker in ice.    1. Crystals will reform but soluble impurities will remain in solution. They are present in small quantities so not saturated. 4. Suction filtrate with a buchner flask to separate out crystals. 5. Wash the crystals with distilled water.    1. To remove soluble impurities 6. Dry the crystals between absorbent paper |
| **By what 3 ways is yield lost under recrystallisation?** | 1. Crystals lost when filtering/washing. 2. Some product stays in solution afterwards. 3. Side reactions occurring. |
| **How is the solvent for recrystallisation chosen? Why? Otherwise what happens?** | * Solvent for which the product is very soluble in hot solvent yet nearly soluble when cold. * If not soluble enough, hot solvent won’t dissolve it all. * If too soluble in cold solvent, most will remain in solution about cooling giving low yield. |
| **How can measuring melting point of a product indicate purity?** | * A very pure sample will have a sharp melting point (as quoted in data books). * One with impurities may have a **lower melting point** or may **melt over a range** of several degrees. |
| **Give 2 ways melting point can be measured with a precaution** | 1. Using an electronic melting point machine. 2. Putting a capillary tube (with the product inside) into heating oil with a thermometer.  * Heat slowly near melting point to record accurate temperature when it **JUST** melts. |
| **Describe the usual set up for determining melting point** | * Thermometer and capillary tube strapped together. * Heating oil with boiling point higher than sample and low flammability. * Constant stirring. |

# 6.3 Analysis

## 6.3.1 - Chromatography and qualitative analysis

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| **What are the 2 phases in chromatography?** | * Stationary phase - the solid on solid support (as in TLC) or liquid on solid support (as in GC). * Mobile phase - liquid or gas. |
| **How does adsorption and solubility affect chromatography?** | * Adsorption - mobile phase interacts with surface by adsorption. More adsorption ⇒ more interaction ⇒ less distance travelled. * Solubility - if stationary phase polar and mobile is nonpolar, nonpolar passes quicker as less soluble. |
| **What problems are there with TLC and GC? Why?** | Distance moved by compound / distance moved by solvent.    *This case uses an amino acid.*  *Each substance has its own unique retention factor.* |
| **What problems are there with TLC and GC? Why?** | Some substances won’t separate since they have similar retention factors / retention times ∵ they're structurally similar.  *It is often used alongside mass spectroscopy.* |
| **What 3 factors affect retention TIMES? And why?** | 1. Solubility - how long each component spends moving along tube (highly soluble will take longer). 2. Boiling point - a substance with a high boiling point will spend more time condensed as a liquid than a gas (taking longer). 3. Temperature of gas chromatography instrument - high means more evaporated as gas so move quickly. |
| **Describe the setup of gas chromatography (GC)** | * Mobile phase is a mixture of gas. * Stationary phase is high b.p. liquid coating the column. |
| **How do you interpret a gas chromatogram?** | * Time taken to pass via column / retention time is used to identify substance. * Area under each peak is proportional to amount of substance (called peak integration value). |
| **What is a calibration curve?** | A curve relating peak areas to concentrations. |
| **How is a calibration curve set up?** | 1. Prepare several standard solutions of known concentrations. 2. Obtain gas chromatograms for each standard solution. 3. Plot a calibration curve of peak area against concentration. |
| *Many of the functional groups tests are elsewhere, the ones which aren’t are below.* | |

## 6.3.2 - Spectroscopy

*Few cards since this is primarily a skill.*

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| **What are equivalent carbons? How do they show up in 13C NMR?** | There is one signal peak for each set of equivalent carbons. |
| **How do equivalent hydrogens differ from equivalent carbons?** | The intensity (peak integration value) ∝ number of equivalent H’s it represents. Eg, |
| **How and why must samples be dissolved in 1H NMR? (with examples)** | Dissolved in solvents without any 1H’s (eg, CCl4 and CDCl3) meaning no interference. |
| **How are both types of NMR calibrated?** | By adding a small amount of TMS (tetramethylsilane). |
| **Why is TMS used in calibrating both types of NMR?** | 1. Non-toxic. 2. Inert. 3. Low b.p. so easily removed afterwards. 4. Signal is far away from others. |
| **What does chemical shift / δ represent in NMR?** | It is how far the frequency of signal is shifted from TMS measured in parts per million (ppm). |
| **How does electronegativity affect 1HNMR?** | If a 1H is closer to more electronegative group, greater shift (further left). |
| **What is the issue with identifying -OH and -NH groups in 1H NMR? How is this solved?** | * They’re very variable and don’t split.  1. Run two spectra of the molecule - one with D2O added. 2. If -OH, -NH present, it’ll swap proton as shown below:   Eg, CH3CH2OH + D2O → CH3CH2OD + HOD  *This works since deuterium doesn’t absorb radio since even number of nucleons.* |
| **What is spin-spin coupling in high-resolution NMR?** | * Each signal can be split based on how many neighbouring **NON-EQUIVALENT** 1H’s (neighbouring means within 3 bonds). * Yet, hydrogens bonded to nitrogen or oxygen don't split or are themselves split.      * Split number of peaks = number of nonequivalent 1H’s within 3 bonds + 1   *The relative sizes follow Pascal’s triangle.* |
| **What table should be drawn for 1H NMR?** | |  |  |  |  |  | | --- | --- | --- | --- | --- | | **Chemical shift / ppm** | **Type of 1H environment** | **Relative 1H’s** | **Assignment** | **Splitting** | | *Range* | *Structure* | *Number* | *Colour / Shape* | *No. Peaks* | |