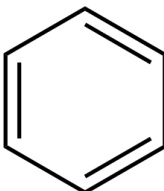
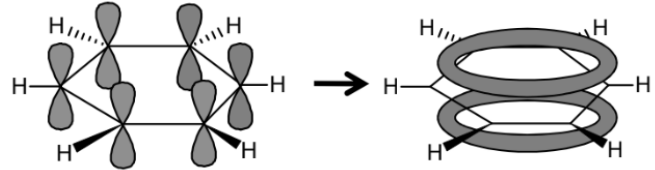
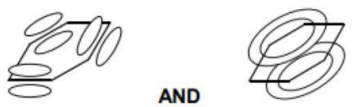
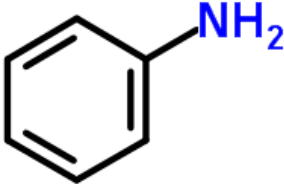
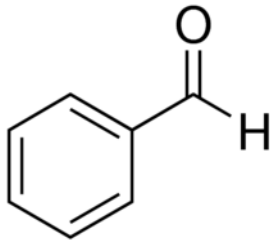
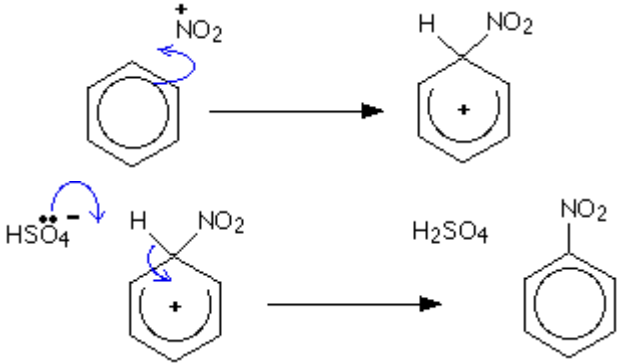


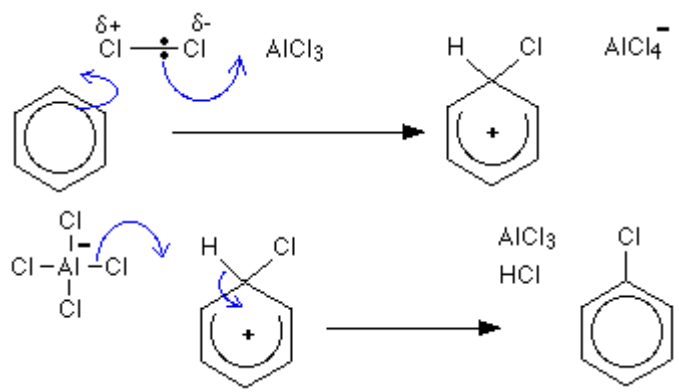
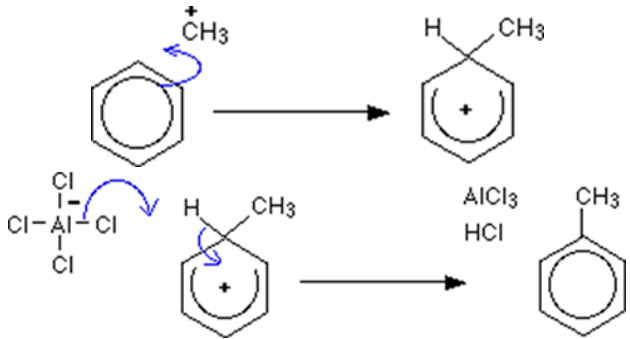
6.1 - Aromatic compounds, carbonyls and acids

6.1.1 - Aromatic compounds

<p>What was wrong with Kekule's benzene structure and why?</p> 	<ul style="list-style-type: none"> Doesn't react readily with halogens... <ul style="list-style-type: none"> 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... <ul style="list-style-type: none"> 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... <ul style="list-style-type: none"> 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.
<p>Describe the π-ring in benzene and its consequences</p>	 <ol style="list-style-type: none"> Sideways overlap of 6 p-orbitals (each containing 1 e⁻). Electron density above and below the plane spread over 6 ¹²C's ∴ low electron density ∴ unable to polarise many molecules ∴ reactions require catalysts. Delocalised electrons meaning not attached to any single atom.
<p>How do these structures compare?</p>  <p style="text-align: center;">AND</p>	<ul style="list-style-type: none"> π-bond(s) are localised between 2 carbons in left structure (1) π-bond(s) are delocalised in right structure (1)

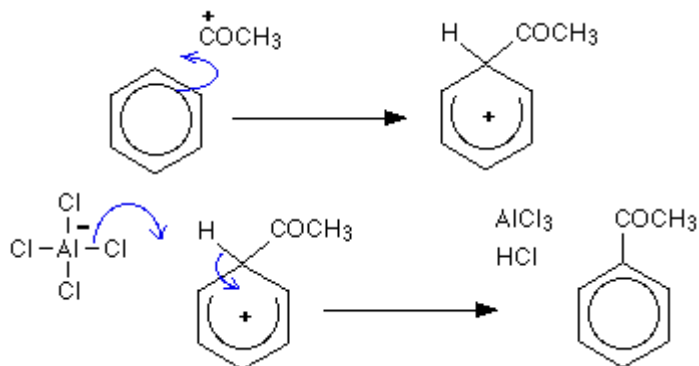
<p>Why are the carbon-carbon bonds in benzene all equal in length?</p>	<p>As the π bonds in benzene are delocalised.</p>
<p>Describe the nomenclature for polysubstituted arenes</p>	<ul style="list-style-type: none"> The lowest number is given to the lowest position of the alphabet: <div data-bbox="852 457 1156 751" data-label="Chemical-Block"> </div> <p>1-bromo-4-chloro-2-ethylbenzene</p> <ul style="list-style-type: none"> When benzene is attached to an alkyl group with 7 or more carbons <u>OR</u> an alkyl with a functional group on it, it is the substituent: <div data-bbox="862 940 1149 1155" data-label="Chemical-Block"> </div> <p><i>Phenylethanone</i></p> <div data-bbox="802 1213 1203 1392" data-label="Chemical-Block"> </div> <p><i>2-phenylhexane</i></p>
<p>Give the 3 non-systematic arenes you need to know</p>	<div data-bbox="862 1476 1141 1696" data-label="Chemical-Block"> </div> <p><i>Benzoic acid</i></p>

	<div style="text-align: center;">  <p>Phenylamine</p>  <p>Benzaldehyde</p> </div>
<p>What are the conditions, reactants, steps (with mechanism), and precautions of nitration?</p>	<ul style="list-style-type: none"> Conditions/reactants: 50 °C, conc. HNO₃ (nitric acid), conc. H₂SO₄ (sulfuric acid). <ol style="list-style-type: none"> Form the nitronium ion... <ol style="list-style-type: none"> Stage 1: $\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$ Stage 2: $\text{H}_2\text{NO}_3^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O}$ Overall: $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_2\text{O}$ React nitronium ion with benzene... <div style="text-align: center;">  <p><i>The catalyst H₂SO₄ has reformed.</i></p> </div> <ul style="list-style-type: none"> Perform within a water bath ∵ reaction is exothermic. Any temperature too high will lead to polynitration rather than mononitration
<p>What are the reactants and steps (with mechanism) of the halogenation of benzene?</p>	<ul style="list-style-type: none"> Reactants: halogen carrier (e.g., FeBr₃/AlBr₃ for bromination and FeCl₃/AlCl₃ for chlorination) as a catalyst.

	<ol style="list-style-type: none"> The halogen carrier polarises the halogen allowing it to react with the halogen carrier to form a positive electrophile. <ul style="list-style-type: none"> $\text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^-$ React the electrophile with the benzene...  <p><i>A positive electrophile has to be formed because benzene isn't very polarising.</i></p>
<p>What are the conditions, reactants, and mechanism for Friedel–Crafts alkylation of benzene?</p>	<ul style="list-style-type: none"> Conditions: heating under reflux. Reactants: haloalkane with its halogen carrier (e.g., AlCl_3 for CH_3Cl). Mechanism: electrophilic substitution,  <p>The $\text{CH}_3\text{Cl} + \text{AlCl}_3$ forms $[\text{CH}_3]^+ + [\text{AlCl}_4]^-$.</p>
<p>What is an acyl halide?</p>	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{X} \end{array}$ <p>Where R is an alkyl group and X is a halogen.</p>
<p>What are the conditions, reactants, equation, and</p>	<ul style="list-style-type: none"> Conditions: heating under reflux, 50 °C.

mechanism for Friedel–Crafts acylation of benzene?

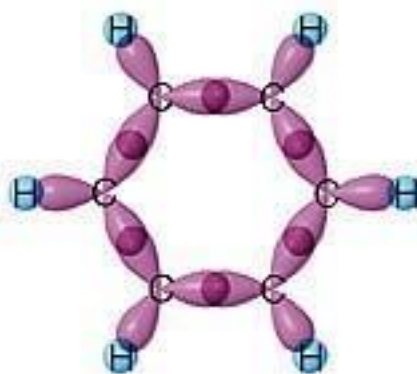
- Reactants: acyl halide and halogen carrier (e.g., CH_3COCl for AlCl_3).
- Equation: $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow [\text{CH}_3\text{CO}]^+ + [\text{AlCl}_4]^-$.
- Mechanism: electrophilic substitution,



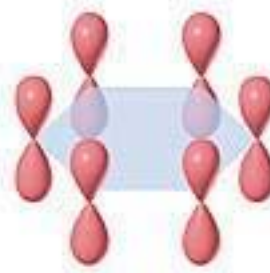
How does benzene compare to other alkenes? (3)

1) Benzene reacts by electrophilic substitution **WHEREAS** other alkenes react by electrophilic addition.

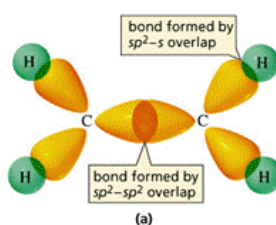
2) Benzene has 6 delocalised e^- 's in π -ring, 12 localised σ e^- 's (2 in each C-C) **WHEREAS** other alkenes have 2 localised e^- 's in π -bond and 2 in σ -bond in $\text{C}=\text{C}$.



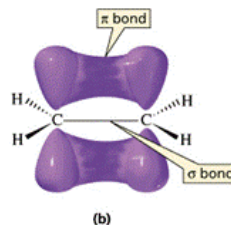
(a) σ bonds



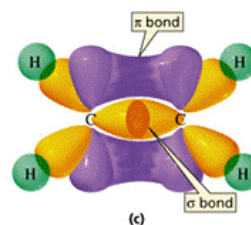
(b) 2p atomic orbitals



(a)


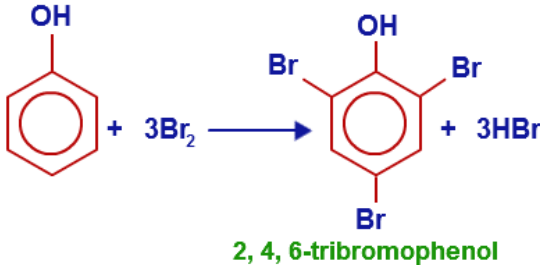


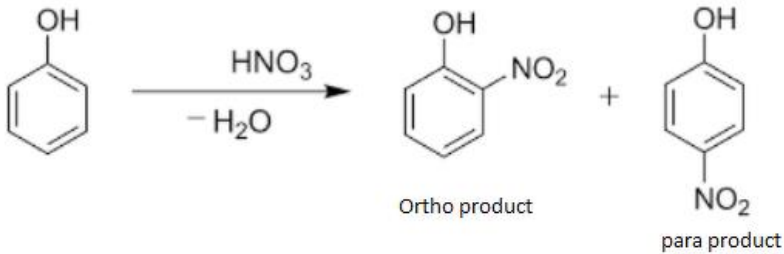
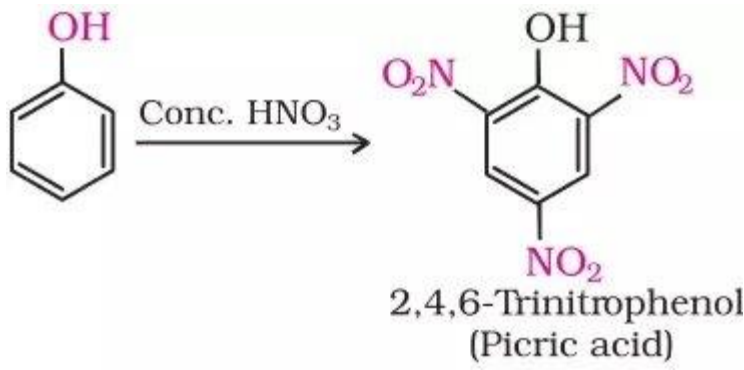
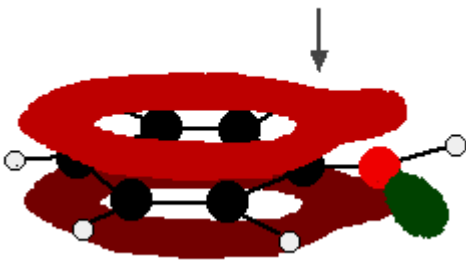
(b)



(c)

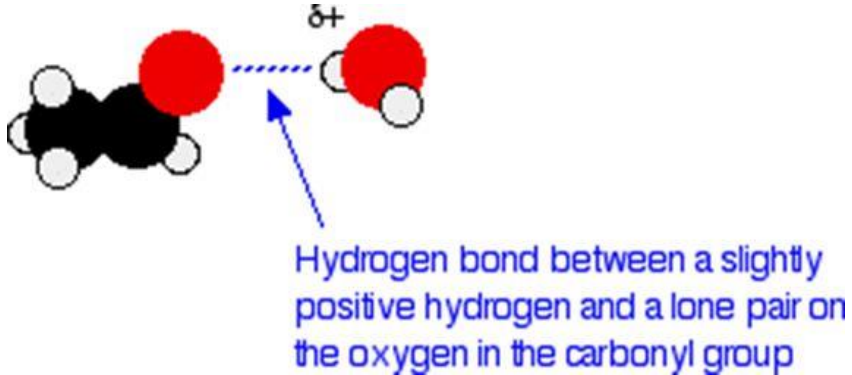
Benzene has 12 σ -bonds in total so 24 σ e^- 's.

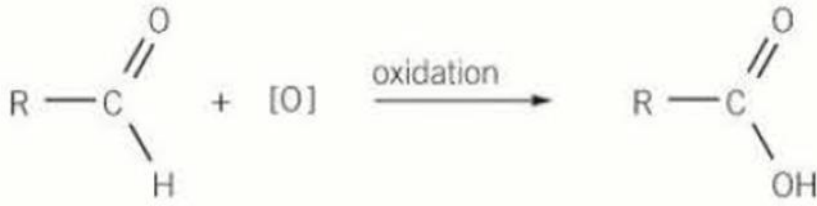
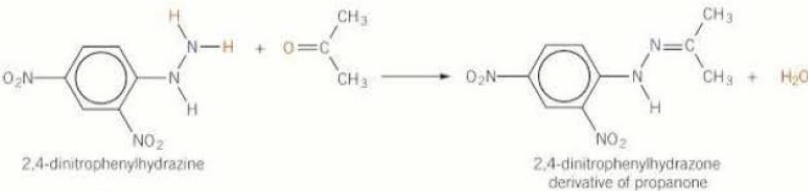
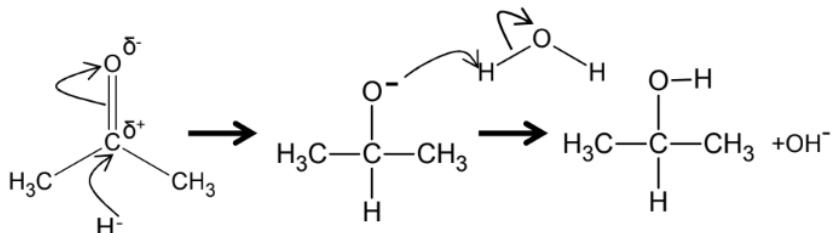
	3) Benzene requires a catalyst (eg, halogen carrier) \therefore its e^- density is too low to polarise molecules WHEREAS other alkenes react readily \therefore high e^- density.
How does the reactivity of methylbenzene and benzene compare?	Methylbenzene is more reactive \therefore alkyl group releases electrons into π -ring \therefore increasing its electron density \therefore more polarising \therefore more reactive.
What is phenol?	A benzene group with a -OH directly attached.
What type of acid is phenol and how will it react with metals and bases?	<p>1. A weak acid.</p> <p>2. Reacts with metals and strong bases (eg, NaOH):</p> <div style="text-align: center;">  <p style="color: red; margin-top: 10px;">sodium phenoxide</p> </div> <p>THIS INCLUDES ANY OTHER AROMATIC COMPOUND WITH AN -OH.</p> <p>3. Too weak to react with weak bases (eg, Na_2CO_3) unlike carboxylic acids.</p>
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., NaCO_3) leading to effervescence HOWEVER phenol will not.
Describe the bromination of phenol (product, conditions, reactants)	<div style="text-align: center;">  <p style="color: green; margin-top: 10px;">2, 4, 6-tribromophenol</p> </div> <ul style="list-style-type: none"> • Forms a white ppt (can be used to distinguish from alkene as the bromine decolourises). • No halogen carrier required, reacts readily, room temperature.

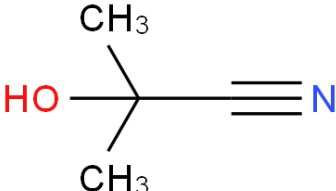
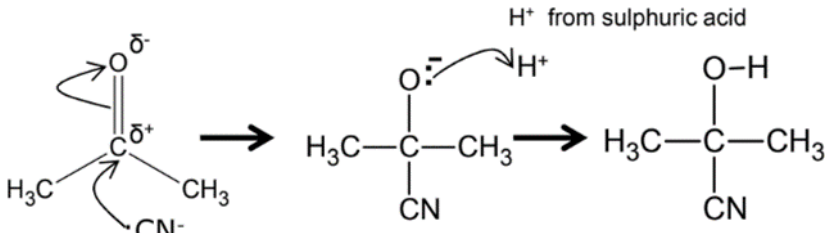
<p>Describe the nitration of phenol (with equation / diagrams)</p>	<p>1. Reacts readily with dilute nitric acid to form a mixture:</p> <div style="text-align: center;">  <p>Ortho product para product</p> </div> <p>2. Reacts readily conc. nitric acid to produce 2,4,6-trinitrophenol:</p> <div style="text-align: center;">  <p>2,4,6-Trinitrophenol (Picric acid)</p> </div>
<p>Why is phenol more reactive than benzene? (3)</p>	<ul style="list-style-type: none"> • The lone pair on the ^{16}O partially delocalises into the π-ring (1) • Electron density increases (1) • Making it more polarising (1) as it includes dipoles making molecules polar. <div style="text-align: center;"> <p>lone pair now delocalised with the ring electrons</p>  </div>
<p>Give 2 uses of phenol</p>	<ul style="list-style-type: none"> • Antiseptic (used by Lister, called carbolic acid). • Detergents. • Dyes.
<p>Describe the 3 cases with 'directing groups' with examples</p>	<p>1. Unsubstituted ring - electron density constant so electrophiles are equally likely to react with any carbon.</p>

	<p>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.</p> <p>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.</p> <p>You can remember -NO₂ as being an electron-withdrawing group since NO for "NOT OPEN".</p>
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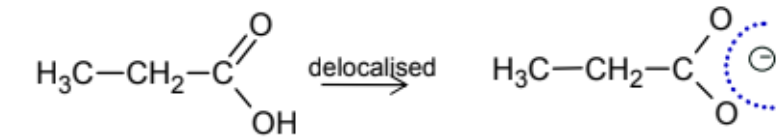
6.1.2 - Carbonyl compounds

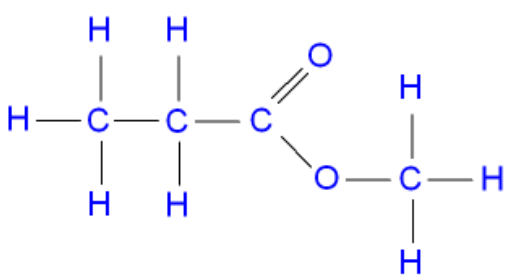
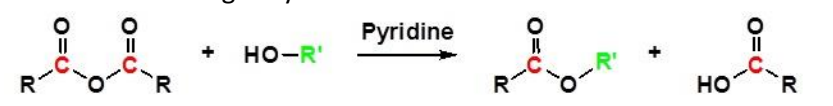
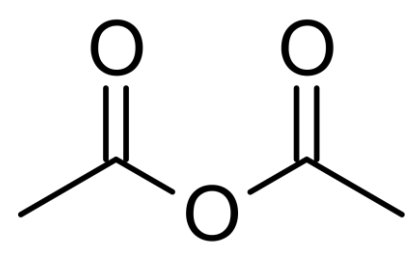
What are carbonyl compounds?	An aldehyde or ketone (containing C=O bond).
Are carbonyls soluble and if so, why and which ones?	<ul style="list-style-type: none"> • Yes as it forms hydrogen bonds. • The small ones. 
How is Tollens' Reagent formed? (aka ammoniacal silver nitrate)	<ol style="list-style-type: none"> 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)	<p>Aldehydes are oxidised by Tollens' into carboxylic acids with Ag⁺ ions being reduced and coating inside of the test tube with a silver mirror:</p> $\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$ <p><u>and</u></p>

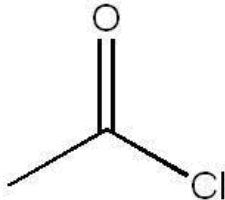
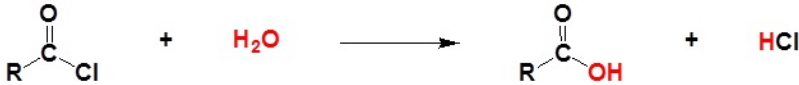
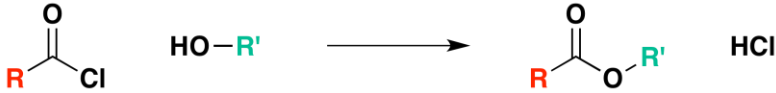
	 <p>This cannot happen with ketones as they cannot be oxidised.</p>
<p>How is Brady's Reagent used to identify carbonyls? And how does it react? (4)</p>	<ul style="list-style-type: none"> Reacts with carbonyls to form a orange/yellow ppt (1)  <p>(2)</p> <ul style="list-style-type: none"> Recrystallise and determine melting point (3) Compare to database values (4)
<p>How are carbonyls reduced to alcohols? (without catalyst method) (reagents, conditions, mechanism, example equation)</p>	<ul style="list-style-type: none"> NaBH₄ is used as a source of hydride (H⁻) ions. In ethanol solution. Mechanism:  <ul style="list-style-type: none"> Examples: <ul style="list-style-type: none"> CH₃CH₂CHO + 2[H] → CH₃CH₂CH₂OH CH₃COCH₃ + 2[H] → CH₃CH(OH)CH₃ <p><i>[H] just means some reducing agent.</i></p>
<p>How can carbonyls be converted to alcohols? (with <u>CATALYST</u>) (type, reagents, conditions, example)</p>	<ul style="list-style-type: none"> Type: reduction. Reagents: H₂ and nickel catalyst. Conditions: high pressure. Examples: CH₃CHO + H₂ → CH₃CH₂OH
<p>What are nitriles?</p>	<p>An organic compound that has a C≡N functional group</p>

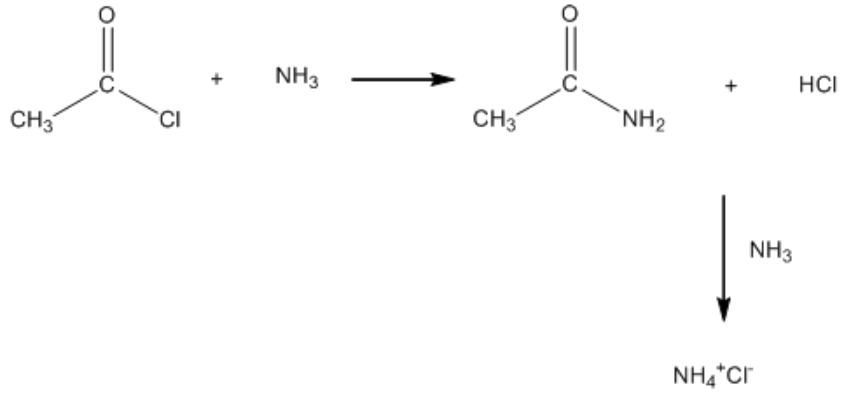
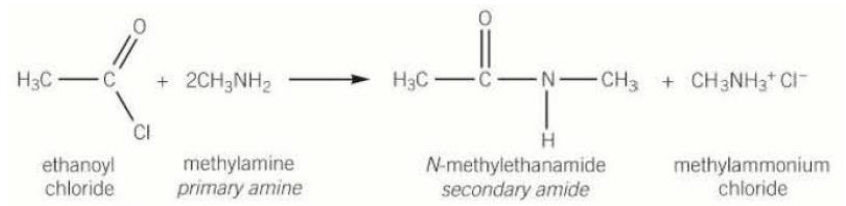
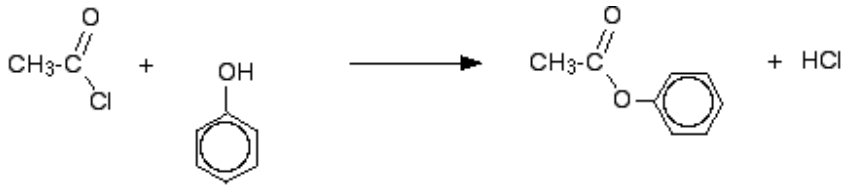
<p>How are nitriles named?</p>	<p>The $\text{C}\equiv\text{N}$ becomes part of the main chain (e.g., 2-hydroxy-2-methylpropanenitrile).</p> 
<p>How can carbonyls become hydroxynitriles and why would you do this? (with reagents, conditions, mechanism)</p>	<ul style="list-style-type: none"> Reagents: sodium cyanide (NaCN) and dilute H_2SO_4 OR HCN. Conditions: RTP. Mechanism: nucleophilic addition. In the case below, NaCN supplies CN^- ions and H_2SO_4 supplies H^+ ions.  <ul style="list-style-type: none"> This is useful for increasing the length of the carbon chain. <p><i>Hydrogen cyanide (HCN) can be used as it dissociates in water to the ions but it's highly toxic.</i></p>

6.1.3 - Carboxylic acids and esters

<p>How does the strength of carboxylic acids vary with carbon chain length and why?</p>	 <p>Alkyl groups electron releasing</p> <ul style="list-style-type: none"> Increasing length means weaker acid. Increasing the length pushes e^- density onto the COO^- making it more negative thus less stable thus less likely to form.
<p>What are salts of carboxylic acids called?</p>	<p>Carboxylates. E.g, $(\text{CH}_3\text{COO}^-)\text{Na}^+$ is called sodium ethanoate.</p>

<p>What is different about methanoic acid to other carboxylic acids?</p>	<p>It can be oxidised as its structure as it has an aldehyde group.</p> $\text{H}-\text{C}(=\text{O})-\text{O}-\text{H} + [\text{O}] \rightarrow \text{H}-\text{O}-\text{C}(=\text{O})-\text{O}-\text{H}$
<p>How are esters named?</p>	<p>The alcohol ends in -yl and is the prefix. The carboxylic acid ends in -anoate and is the suffix.</p>  <p><i>This is called methyl-ethanoate.</i></p>
<p>Describe the 2 types of esterification</p>	<ol style="list-style-type: none"> Esterification using acid catalyst: <ul style="list-style-type: none"> Carboxylic acid + alcohol \rightleftharpoons ester + water Sulfuric acid catalyst required for H^+ ions Heat under reflux Esterification using acid anhydrides: <ul style="list-style-type: none"> Acid anhydride + alcohol \rightarrow ester Room temperature Higher yield achieved <div style="text-align: center;">  <div style="display: flex; justify-content: space-around; margin-top: 5px;"> Acid Anhydride Alcohol Ester Carboxylic acid </div> </div>
<p>What is an acid anhydride?</p>	<p>Two different carboxylic acids joined together.</p>  <p><i>Ethanoic anhydride</i></p>
<p>Give 2 ways esters can be hydrolysed (with conditions)</p>	<ol style="list-style-type: none"> <u>Heating with HOT AQUEOUS ACID:</u> <ul style="list-style-type: none"> Use sulfuric acid catalyst under reflux. Forms the original reactants.

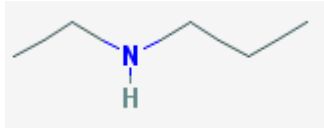
	<ul style="list-style-type: none"> $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH}$ (reversible so doesn't give a good yield) <p>2. Heating with HOT AQUEOUS ALKALI (saponification):</p> <ul style="list-style-type: none"> Use sodium hydroxide under reflux. Forms a carboxylate and alcohol. $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 + \text{NaOH} \rightarrow (\text{CH}_3\text{CH}_2\text{CO}_2^-)\text{Na}^+ + \text{CH}_3\text{OH}$ <p><i>The anion in the salt is resistant to attack by weak nucleophiles such as the alcohol so this reaction isn't reversible.</i></p>
How and why are acyl chlorides better than carboxylic acids?	<p>They are more reactive than carboxylic acids as Cl is a good leaving group.</p> 
How are acyl chlorides formed?	<ul style="list-style-type: none"> By reacting carboxylic acid using SOCl_2 (thionyl chloride). $\text{CH}_3\text{COOH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{COCl} + \text{SO}_2 + \text{HCl}$
How do acyl chlorides react with water?	<p>To produce a carboxylic acid.</p> 
How do acyl chlorides react with alcohols and why is it good?	<ul style="list-style-type: none"> To produce an ester. It's faster (\because more reactive) and not reversible.  <p>Acid Chloride Alcohol Ester HCl</p>
How do acyl chlorides react with ammonia?	<p>To produce a primary amide.</p>

	 $\text{CH}_3\text{COCl} + \text{NH}_3 \longrightarrow \text{CH}_3\text{CONH}_2 + \text{HCl}$ $\text{CH}_3\text{CONH}_2 + \text{NH}_3 \longrightarrow \text{NH}_4^+\text{Cl}^-$
How do acyl chlorides react with primary and secondary amines? (with example equation)	<ul style="list-style-type: none"> To produce secondary and tertiary amides respectively. Example:  <p><i>The N means that the methyl group is bonded to the nitrogen rather than the main carbon chain.</i></p>
How do acyl chlorides react with phenol and why is this used?	<ul style="list-style-type: none"> Form an ester. Phenol doesn't react readily with carboxylic acids. 
What 2 things are common for most reactions of acyl chlorides?	<ol style="list-style-type: none"> Carried out at room temperature. Any HCl (g) is given off at steamy white fumes

6.2 - Nitrogen compounds, polymers and synthesis

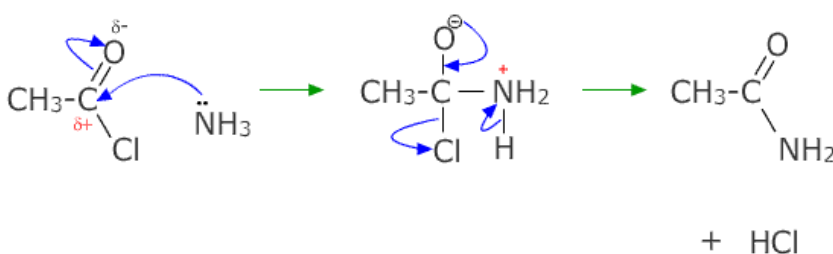
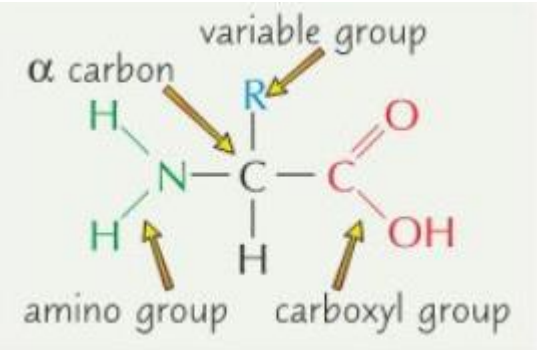
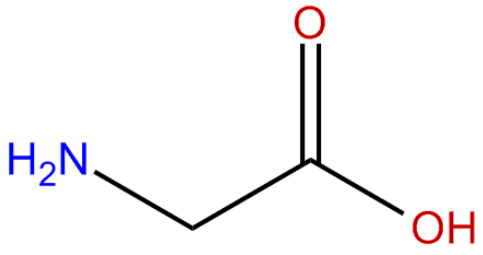
6.2.1 - Amines

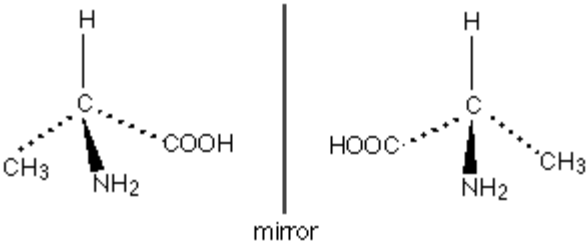
What is an amine?	A compound containing -NH ₂ group.
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	$\begin{array}{c} \text{H}_3\text{C}-\text{N}-\text{CH}_3 \\ \\ \text{H} \end{array}$ <p><i>This is dimethylamine.</i></p>
How do you name amines if the substituent groups aren't the same?	<p>As an N-substituted derivative of the longest carbon chain. Eg, N-ethylpropylamine:</p> 
What do amines primarily react as?	<p>Bases. Eg, they react with HCl to produce methylammonium chloride (a salt)</p> $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{N}: \\ \quad \\ \text{H} \quad \text{H} \end{array} + \text{H}^+ \rightarrow \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{N}^+-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ <p style="text-align: center;">methylamine proton methylammonium ion</p> <p>This equation doesn't include the Cl⁻ ion</p>
How are primary aliphatic amines formed? (with reactants, conditions, and equations)	<ul style="list-style-type: none"> • 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: $\text{CH}_3\text{CH}_2\text{Br} + \text{NH}_3 \longrightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+ \text{Br}^-$ $\text{CH}_3\text{CH}_2\text{NH}_3^+ \text{Br}^- + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4^+ \text{Br}^-$
How are secondary and tertiary aliphatic amines formed? (with reactants, conditions, and equations)	<ul style="list-style-type: none"> • Reactants: haloalkane and primary / secondary amine. • Conditions: ethanol as solvent (preventing hydrolysis of haloalkanes). • Equations:

	$ \begin{array}{ccccccc} \text{R}_1 & & & & \text{R}_1 & & \\ & & & & & & \\ \text{H}-\text{N:} & + & \text{R}_3\text{X} & \longrightarrow & \text{:N}-\text{R}_3 & + & \text{HX} \\ & & & & & & \\ \text{R}_2 & & & & \text{R}_2 & & \\ \text{primary or} & & \text{halogenoalkane} & & \text{alkyl-substituted} & & \text{halogen} \\ \text{secondary} & & & & \text{amine} & & \text{acid} \\ \text{amine} & & & & \text{(secondary} & & \\ & & & & \text{or tertiary)} & & \end{array} $
<p>How is phenylamine formed from nitrobenzene? (conditions, reactants, type of reaction, and equation)</p>	<ul style="list-style-type: none"> • Conditions: reflux. • Reactants: Sn, conc. HCl and excess NaOH (required for hydroxide ions). • Type of reaction: reduction. <div style="text-align: center; background-color: #e6f2ff; padding: 10px; margin: 10px 0;"> <p style="text-align: center;"> $\text{nitrobenzene} + 6[\text{H}] \xrightarrow[\text{(2) NaOH}]{\text{(1) tin, conc. HCl, reflux}} \text{phenylamine} + 2\text{H}_2\text{O}$ </p> </div> <p><i>This catalyst is required as -NO₂ is an electron-withdrawing group so lowers electron density.</i></p> <p><i>This is because during step 1, we have the H⁺ ions from the HCl and the e⁻s from the Sn forming phenylammonium.</i></p> <div style="text-align: center; margin: 10px 0;"> <p style="text-align: center;"> $\text{nitrobenzene} + 7\text{H}^+ + 6\text{e}^- \longrightarrow \text{phenylammonium ion} + 2\text{H}_2\text{O}$ </p> </div> <p><i>Then in the step 2, we have the HO⁻ reacting to form phenylamine.</i></p> <div style="text-align: center; margin: 10px 0;"> <p style="text-align: center;"> $\text{phenylammonium ion} + \text{OH}^- \longrightarrow \text{phenylamine} + \text{H}_2\text{O}$ </p> </div>

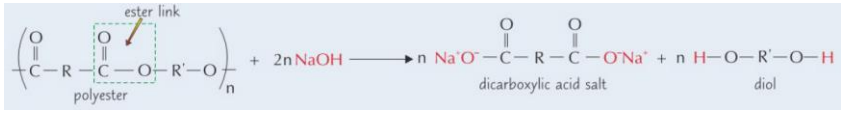
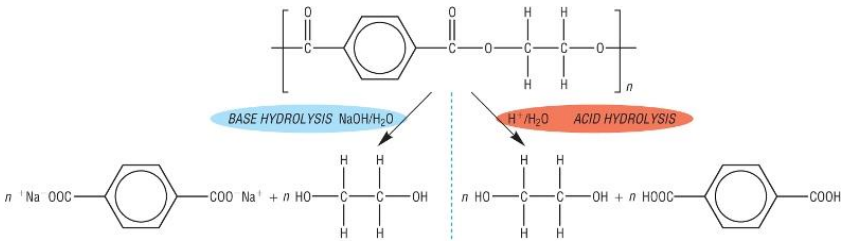
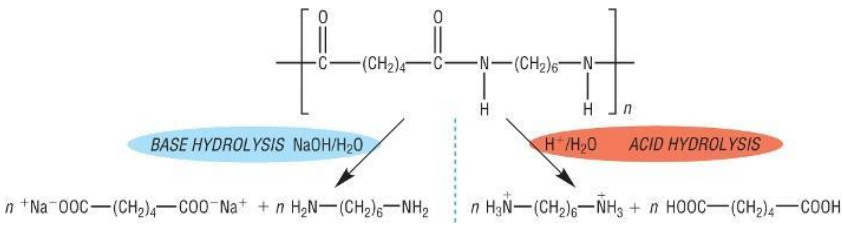
6.2.2 - Amino acids, amides and chirality

What are amides?	A compound containing a -CONH ₂ group.
How are primary amides formed? What precaution must be taken?	<ul style="list-style-type: none"> By reacting acyl chlorides with ammonia.  $\text{CH}_3\text{-C}(=\text{O})\text{Cl} + \text{NH}_3 \rightarrow \text{CH}_3\text{-C}(=\text{O})\text{NH}_2 + \text{HCl}$ <ul style="list-style-type: none"> You require a lot of NH₃ to react with HCl to allow the reaction to go to completion.
What are amino acids?	A central carbon with an amino group and carboxyl group. 
How are amino acids named?	 <p>(2-)aminoethanoic acid</p>
What are optical isomers and what is required of them?	<ul style="list-style-type: none"> Stereoisomers that are non-superimposable mirror images. 4 different groups attached to a carbon (called the chiral centre).

	 <p>There are enantiomers / optical isomers.</p> <ul style="list-style-type: none"> - They can be referred to as both 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.
How are primary amides converted to carboxylic acids? (reagents, type of reaction, equation)	<ul style="list-style-type: none"> • Reagents: HCl (aq) • Type of reaction: acid hydrolysis • Equation: $\text{CH}_3\text{CONH}_2 + \text{H}_2\text{O} + \text{HCl} \rightarrow \text{CH}_3\text{COOH} + \text{NH}_4^+\text{Cl}^-$

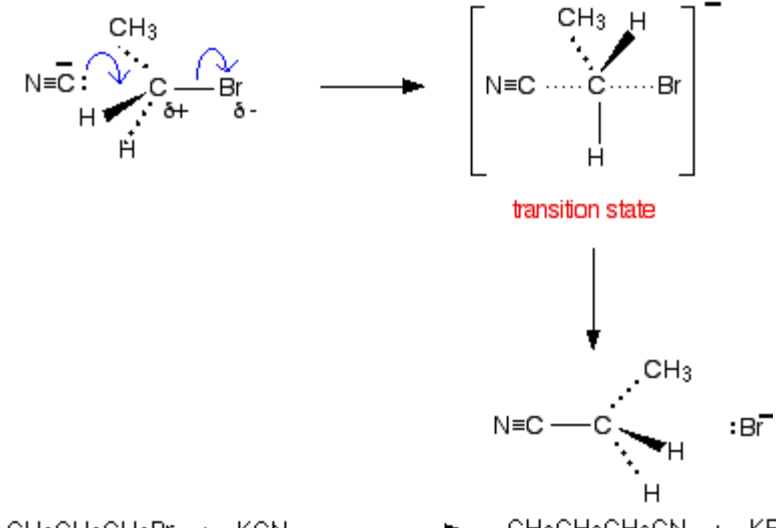
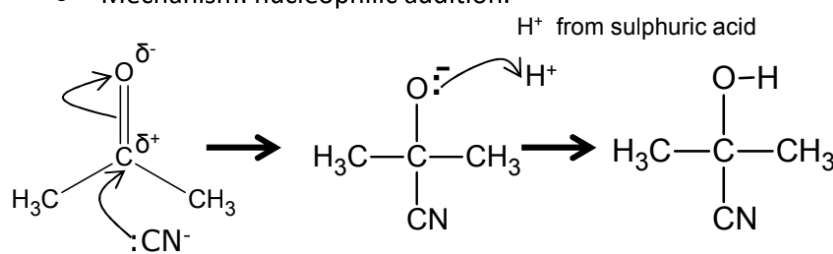
6.2.3 - Polyesters and polyamides

What are the 2 types of polymerisation?	<ol style="list-style-type: none"> 1. Addition polymerisation. 2. Condensation polymerisation.
What is addition polymerisation?	When unsaturated monomers react.
What is condensation polymerisation?	<p>Two different monomers that add together with a small molecule usually given off as a side-product (eg, H_2O or HCl).</p> <p><i>These monomers usually have the same functional group on both ends of the molecule (eg, diamine, dicarboxylic acid, diol, diacyl chloride).</i></p>
Give the 2 most common types of condensation polymers with their linkage	<ol style="list-style-type: none"> 1. Poly(esters) which contain an ester link ($-\text{COO}-$). 2. Poly(amides) which contain an amide link ($-\text{CONH}-$). <p>They form what is called an ester linkage or amide linkage.</p>

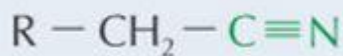
How and why are polyester and polyamides biodegradable?	<ul style="list-style-type: none"> They can be broken down by hydrolysis. Due their polar nature attracting attacking species.
Why may condensation polymers be photodegradable?	As the C=O bond absorbs radiation.
What are condensation polymers hydrolysed by? In what is each hydrolysed more easily?	<ul style="list-style-type: none"> Hot (aq) acid or alkali. Poly(<u>a</u>mides) are hydrolysed more easily with strong <u>a</u>cid. Poly(esters) are hydrolysed more easily with strong bases.  <p><i>It can be hydrolysed by water but it's FAR too slow.</i></p>
What does the base and acid hydrolysis of poly(esters) yield?	 <ol style="list-style-type: none"> Base - dicarboxylate salt and diol. Acid - dicarboxylic acid and diol.
What does the base and acid hydrolysis of poly(amides) yield?	 <ol style="list-style-type: none"> Base - dicarboxylate salt and diamine. Acid - dicarboxylic acid and diammonium.

6.2.4 - Carbon-carbon bond formation

What are the reagents, conditions, mechanism for converting a haloalkane to nitrile?	<ul style="list-style-type: none"> Regant: :CN⁻ (from NaCN / KCN) Conditions: heating under reflux, dissolved in ethanol (since water will form alcohols) Mechanism: nucleophilic substitution,
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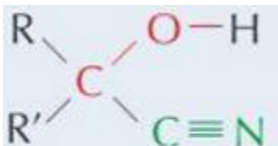
	 <p style="text-align: center;">$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{KCN} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} + \text{KBr}$</p>
<p>What are the reagents, conditions, mechanism for converting a carbonyl to hydroxynitrile?</p>	<ul style="list-style-type: none"> • Reagents: :CN^- (from NaCN / KCN dissolved in ethanol since water will form alcohols) and dilute sulfuric acid. • Conditions: RTP. • Mechanism: nucleophilic addition.  <p>H^+ ion is supplied by H_2SO_4.</p> <p><i>HCN could be used yet it is a toxic gas and is difficult to gain.</i></p>
<p>What are the possible reagents and type of reaction for converting nitriles to amines? (with example)</p>	<ul style="list-style-type: none"> • Reagents: LiAlH_4 <u>OR</u> H_2 with Ni catalyst. • Type: reduction. • Examples: $\text{CH}_3\text{CN} + 4[\text{H}] \longrightarrow \text{CH}_3\text{CH}_2\text{NH}_2$ $\text{CH}_3\text{CN} + 2\text{H}_2 \xrightarrow{\text{Pd}} \text{CH}_3\text{CH}_2\text{NH}_2$ <p><i>This particular example uses a different catalyst.</i></p>
<p>What are the reagents, conditions, type of reaction, and examples for converting (hydroxy-)nitriles to carboxylic acids?</p>	<ul style="list-style-type: none"> • Reagents: dilute acid (eg, dilute HCl). • Conditions: heating under reflux. • Type: hydrolysis. • Examples:

Examples:

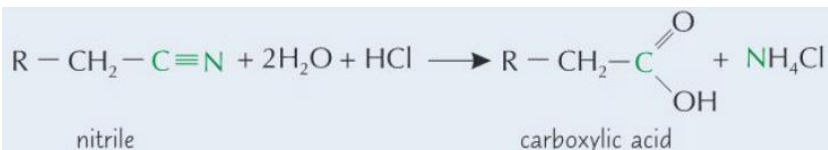


nitrile

and



hydroxynitrile



6.2.5 - Organic synthesis

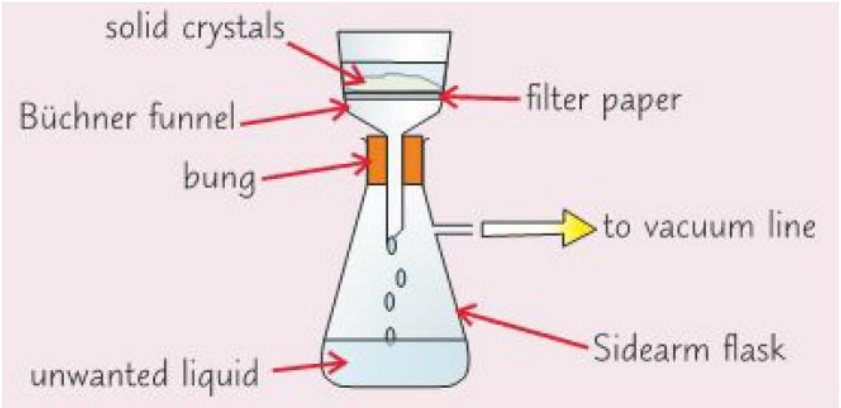
You can learn the synthesis routes by learning the other flashcards.


Covered distillation and reflux.

How can you purify an organic liquid?

1. **Pour** the distillate (something formed from distillation) of impure product into a separating funnel.
2. **Wash** with:
 - a. NaHCO_3 solution **TO NEUTRALISE ANY ACID IMPURITIES**, shake, and release pressure from CO_2 produced.
 - b. Saturated NaCl solution to separate layers.
3. **Allow** layers to separate and discard aqueous layer (the organic layer will be on top usually due to a 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.
7. **Redistill** to collect pure product.

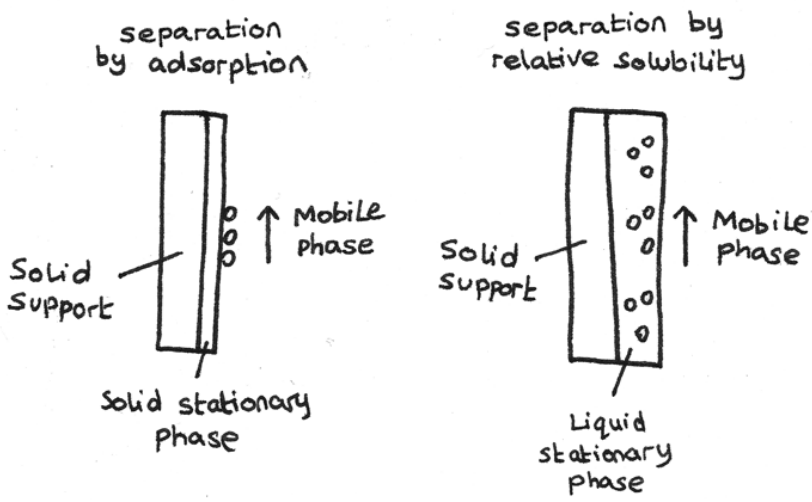
Decant means carefully pour off organic liquid leaving the drying agent in the conical flask.

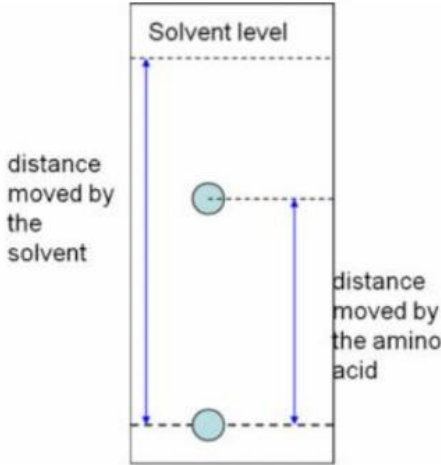
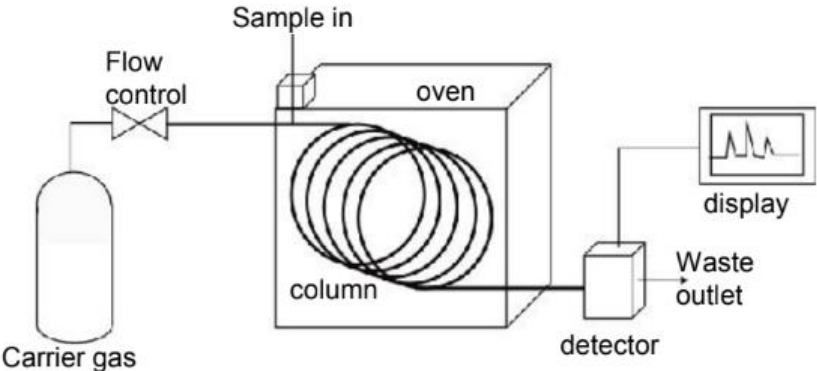
<p>What should you ensure with the drying agent for purifying organic liquids?</p>	<ul style="list-style-type: none"> • Be insoluble in the organic liquid. • Not react with the organic liquid.
<p>How can you purify an organic solid by recrystallisation? Why is each step used?</p>	<ol style="list-style-type: none"> 1. <u>Dissolve</u> impure compound in minimum volume of hot solvent. <ol style="list-style-type: none"> a. To ensure saturated solution. 2. <u>Filter</u> using filter paper quickly. <ol style="list-style-type: none"> a. Removing any insoluble impurities. 3. <u>Cool</u> filtered solution by inserting beaker in ice. <ol style="list-style-type: none"> a. Crystals will reform but soluble impurities will remain in solution. They are present in small quantities so not saturated. 4. <u>Scratch</u> with glass rod to initiate crystallisation. 5. <u>Suction</u> filtrate with a buchner flask to separate out crystals. 6. <u>Wash</u> the crystals with COLD solvent (otherwise it will dissolve in hot). <ol style="list-style-type: none"> a. To remove soluble impurities. 7. <u>Dry</u> the crystals between absorbent paper. <p>REMEMBER THIS AS DFCSSWD: Deaf Fruity Crayons Scramble Standard Warm Distances.</p> 
<p>By what 3 ways is yield lost under recrystallisation?</p>	<ol style="list-style-type: none"> 1. Crystals lost when filtering/washing. 2. Some product stays in solution afterwards. 3. Side reactions occurring.
<p>How is the solvent for recrystallisation chosen? Why? Otherwise what happens?</p>	<ul style="list-style-type: none"> • A solvent in which the product (to be purified) is very soluble when solvent is hot and nearly insoluble when cold. • If not soluble enough, hot solvent won't dissolve it all.

	<ul style="list-style-type: none"> 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?	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> Using an electronic melting point machine. 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	 <p>Capillary tube with sample</p> <p>Thin ring cut from rubber or plastic tubing</p> <p>Oil bath</p> <p>Heat here</p> <p>(a)</p> <ul style="list-style-type: none"> Thermometer and capillary tube strapped together. Heating oil with boiling point higher than sample and low flammability. Constant stirring.
What problems are there with producing chiral drugs? How is it solved?	<p>Problems:</p> <ul style="list-style-type: none"> Separation is expensive. Can have different effects than intended. <p>Solutions:</p> <ul style="list-style-type: none"> Use chiral synthesis. Use a chiral catalyst.

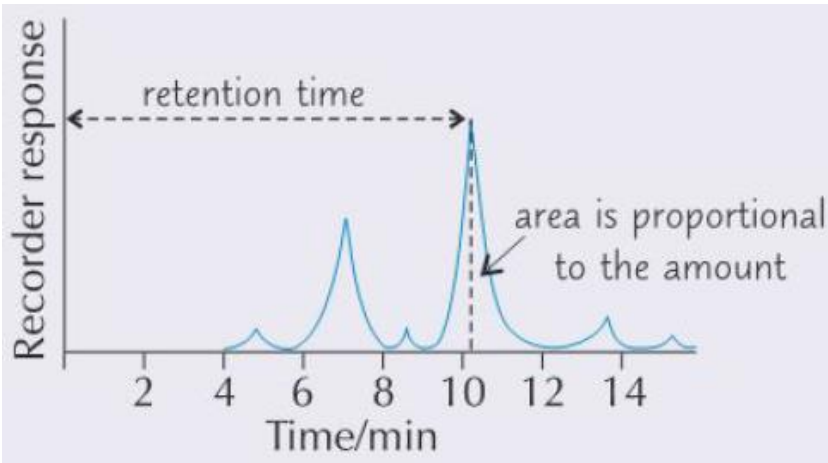
6.3 Analysis

6.3.1 - Chromatography and qualitative analysis

<p>What are the 2 phases in chromatography?</p>	<ul style="list-style-type: none"> • Stationary phase - the solid on solid support (as in TLC) or liquid on solid support (as in GC). • Mobile phase - liquid (as in TLC) or gas (as in GC). <div style="text-align: center;">  </div> <p><i>TLC is shown on the left whereas GC is shown on the right.</i></p>
<p>How does adsorption and solubility affect chromatography? (include polarity)</p>	<ol style="list-style-type: none"> 1. Adsorption: <ol style="list-style-type: none"> a. Mobile phase interacts with surface of stationary phase by adsorption. b. More adsorption \Rightarrow more interaction \Rightarrow travels slower / less distance. 2. Solubility: <ol style="list-style-type: none"> a. If mobile phase is nonpolar and stationary phase is polar \Rightarrow less soluble \Rightarrow passes quicker.
<p>What problems are there with TLC and GC? Why?</p>	<ul style="list-style-type: none"> • Distance moved by compound / distance moved by solvent. • By comparing to database values.

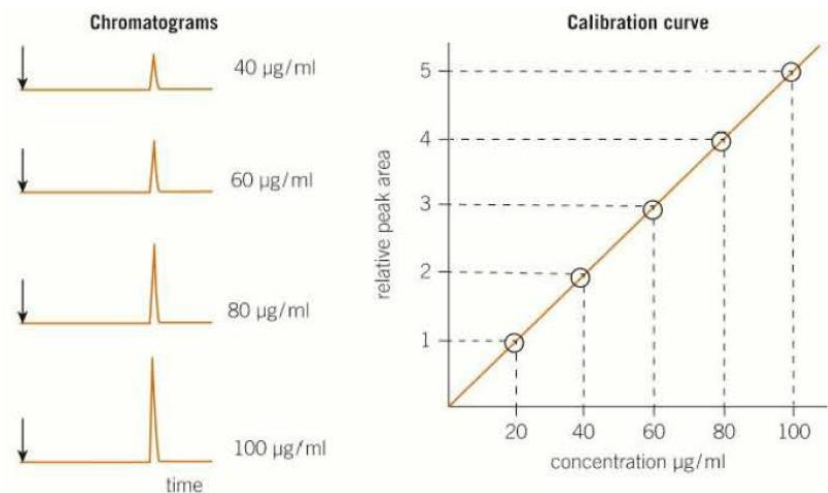
	 <p style="text-align: center;"><i>This case uses an amino acid.</i></p> <p style="text-align: center;"><i>Each substance has its own unique retention factor.</i></p>
<p>What problems are there with TLC and GC? Why?</p>	<p>Some substances won't separate since they have similar retention factors / retention times ∴ they're structurally similar.</p> <p><i>It is often used alongside mass spectroscopy.</i></p>
<p>What 3 factors affect retention <u>TIMES</u>? And why?</p>	<ol style="list-style-type: none"> 1. <u>Solubility</u> - more soluble compounds will take longer to move via the tube. 2. <u>Boiling point</u> - a substance with a high boiling point will spend more time condensed as a liquid than a gas (taking longer). 3. <u>Temperature</u> of gas chromatography instrument - high means more evaporated as gas so move quickly.
<p>Describe the setup of gas chromatography (GC)</p>	 <ul style="list-style-type: none"> • 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.

What does a liquid stationary phase separate organic compounds by?
















By relative solubility.

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.

<p>What are equivalent carbons? How do they show up in ^{13}C NMR?</p>	<p>Carbons which are in the same environment.</p> <div style="text-align: center;"> <p>5 peaks 2 peaks</p> </div> <p>There is one signal peak for each set of equivalent carbons.</p>
<p>How do equivalent hydrogens differ from equivalent carbons?</p>	<p>The intensity (peak integration value) \propto number of equivalent H's it represents. Eg,</p> <div style="text-align: center;"> </div>
<p>How and why must samples be dissolved in ^1H NMR? (with examples)</p>	<p>Dissolved in solvents without any ^1H's (eg, CCl_4 and CDCl_3) meaning no interference.</p>
<p>How are both types of NMR calibrated?</p>	<p>By adding a small amount of TMS (tetramethylsilane).</p>
<p>Why is TMS used in calibrating both types of NMR?</p>	<ol style="list-style-type: none"> 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 ^1H NMR?	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?	<ul style="list-style-type: none">They're very variable and don't split. <ol style="list-style-type: none">Run two spectra of the molecule - one with D_2O added.If -OH, -NH present, it'll swap proton as shown below: <p>Eg, $\text{CH}_3\text{CH}_2\text{OH} + \text{D}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OD} + \text{HOD}$</p> <ul style="list-style-type: none">This is called <u>PROTON EXCHANGE</u>. <p><i>This works since deuterium doesn't absorb radio since even number of nucleons.</i></p>																														
What is spin-spin coupling in high-resolution NMR?	<ul style="list-style-type: none">Each signal can be split based on how many neighbouring <u>NON-EQUIVALENT</u> ^1H's (neighbouring means within 3 bonds).Yet, hydrogens bonded to nitrogen or oxygen don't split or are themselves split. <table><tr><td>signal</td><td>singlet</td><td>doublet</td><td>triplet</td><td>quartet</td><td>quintet</td></tr><tr><td>appearance</td><td></td><td></td><td></td><td></td><td></td></tr><tr><td>Split number of peaks</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td></tr><tr><td>number of neighbouring inequivalent H atoms</td><td>0</td><td>1</td><td>2</td><td>3</td><td>4</td></tr><tr><td>relative size</td><td></td><td>1:1</td><td>1:2:1</td><td>1:3:3:1</td><td>1:4:6:4:1</td></tr></table> <ul style="list-style-type: none">Split number of peaks = number of nonequivalent ^1H's within 3 bonds + 1 <p><i>The relative sizes follow Pascal's triangle.</i></p>	signal	singlet	doublet	triplet	quartet	quintet	appearance						Split number of peaks	1	2	3	4	5	number of neighbouring inequivalent H atoms	0	1	2	3	4	relative size		1:1	1:2:1	1:3:3:1	1:4:6:4:1
signal	singlet	doublet	triplet	quartet	quintet																										
appearance																															
Split number of peaks	1	2	3	4	5																										
number of neighbouring inequivalent H atoms	0	1	2	3	4																										
relative size		1:1	1:2:1	1:3:3:1	1:4:6:4:1																										

What table should be drawn for ^1H NMR?					
	Chemical shift / ppm	Type of ^1H environment	Relative ^1H 's	Assignment	Splitting
	<i>Range</i>	<i>Structure</i>	<i>Number</i>	<i>Colour / Shape</i>	<i>No. Peaks</i>