

Edexcel Chemistry A-level

Topic 18 - Organic Chemistry III

Flashcards

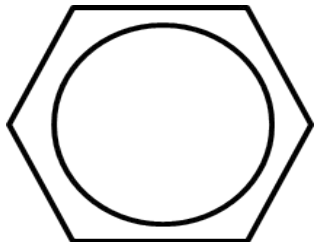
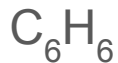
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What is benzene's formula and structure?



What is the formula and structure of benzene?



What is another name for arenes? Why did this come about?



What is another name for arenes? Why did this come about?

Aromatic compounds, as first found in sweet-smelling dyes



What is the most common type of reaction of benzene?



What is the most common type of reaction of benzene?

Substitution (of a H for a different functional group)



What is the shape of benzene?



What is the shape of benzene?

Flat, regular hexagon. Bond angle = 120°



What is the bond length
between adjacent C atoms?



What is the bond length between adjacent C atoms?

Intermediate between C-C and C=C



What happens to the 4th electron in the p orbital of each C atom in benzene?



What happens to the 4th electron in the p orbital of each C atom in benzene?

It delocalises to form rings of electron density above and below the hexagon, forming rings of delocalised electron density above/below the hexagon.



What is the effect on the stability of the rings of benzene on electron density?



What is the effect on the stability of the rings of benzen on electron density?

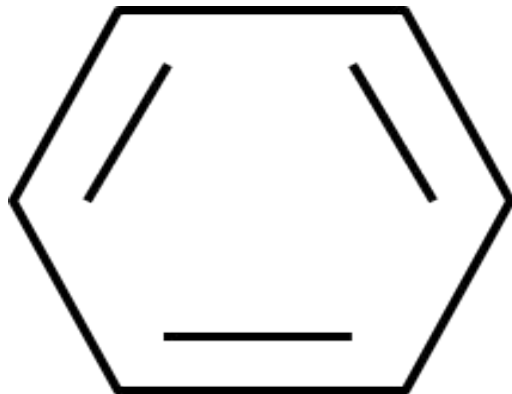
Makes benzene very stable, even though it is unsaturated (aromatic stability)



Draw the skeletal structure
of cyclohexa-1,3,5-triene



Draw the skeletal structure of cyclohexa-1,3,5-triene



What is the thermochemical evidence that benzene is more stable than cyclohexa-1,3,5-triene?



What is the thermochemical evidence that benzene is more stable than cyclohexa-1,3,5-triene?

Hydrogenation of cyclohexene = -120kJmol^{-1} →

cyclohexa-1,3,5-triene = -360kJmol^{-1}

Benzene hydrogenation = -208kJmol^{-1} so

benzene is 152kJmol^{-1} more stable



Why else is
cyclohexa-1,3,5-triene not a
suitable model for benzene?



Why else is cyclohexa-1,3,5-triene not a suitable model for benzene?

Would not be symmetrical (C=C shorter than C-C), but benzene is

Would easily undergo addition reactions across the double bonds - benzene does not

Would form two isomers on the addition of Br₂ or similar - benzene does not



What is the appearance of benzene at 298K?



What is the appearance of benzene at 298K?

Colourless liquid



Why does benzene have a relatively high melting point?



Why does benzene have a relatively high melting point?

Close packing of flat hexagonal molecules when solid



Is benzene soluble in water? Why?



Is benzene soluble in water? Why?

No- non polar



Dangers of benzene? (why it is not used in schools)



Dangers of benzene? (why it is not used in schools)

It is a carcinogen



How do you name
compounds containing a
benzene ring?



How do you name compounds containing a benzene ring?

-benzene, or phenyl- ; can designate position on ring using numbers if there is more than one substituent



Why is benzene attacked by electrophiles?



Why is benzene attacked by electrophiles?

High electron density above/below ring due to delocalised electrons



What is delocalisation energy and what is the effect of this on the reactions on benzene?



What is delocalisation energy and what is the effect of this on the reactions of benzene?

The large amount of energy that is needed to break the aromatic ring apart. Results in the aromatic ring almost always staying intact



What is seen when benzene is combusted? Why?



What is seen when benzene is combusted? Why?

Smoky flames due to soot from unburnt carbon.

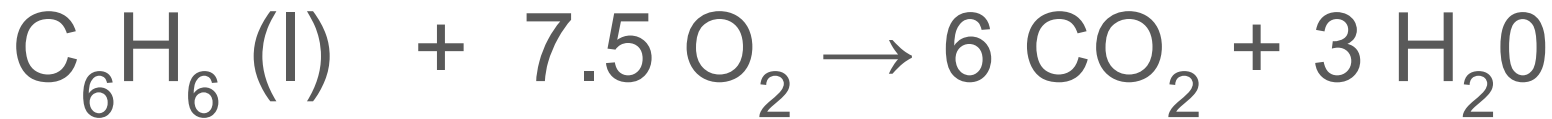
This is because of the high Carbon:Hydrogen ratio.



Write an equation of the
reaction between benzene
and oxygen



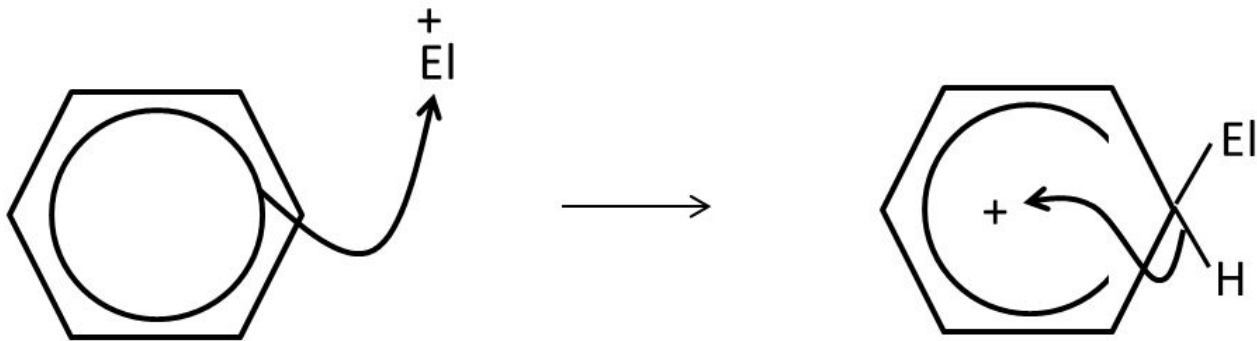
Write an equation of the reaction between benzene and oxygen



Draw a general electrophilic substitution mechanism of benzene, using EI^+ to represent an electrophile.



Draw a general electrophilic substitution mechanism of benzene, using EI^+ to represent an electrophile



Which ion (name and formula) is used to nitrate benzene?



Which ion (name and formula) is used to nitrate benzene?

NO_2^+ (+ charge is on the nitrogen). Nitronium ion or nitryl cation

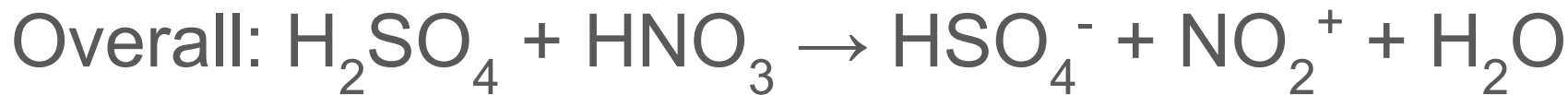


How is this NO_2^+ ion
generated? (conditions and
equations)



How is this NO_2^+ ion generated? (conditions and equations)

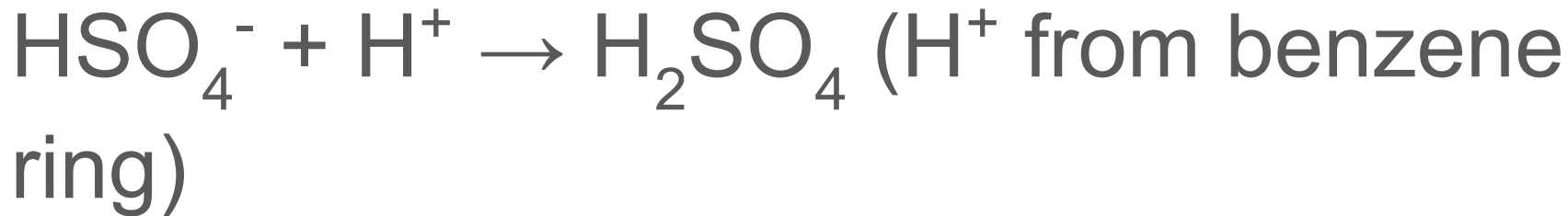
Concentrated H_2SO_4 and concentrated HNO_3 .



How is the H_2SO_4 catalyst regenerated in the nitration of benzene?



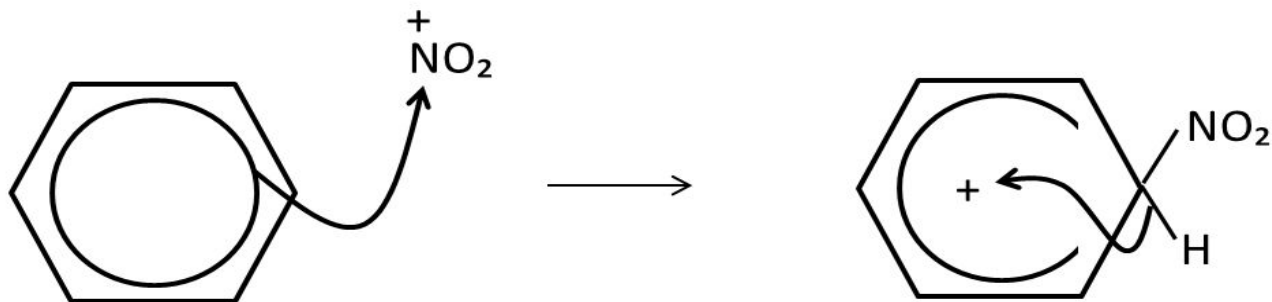
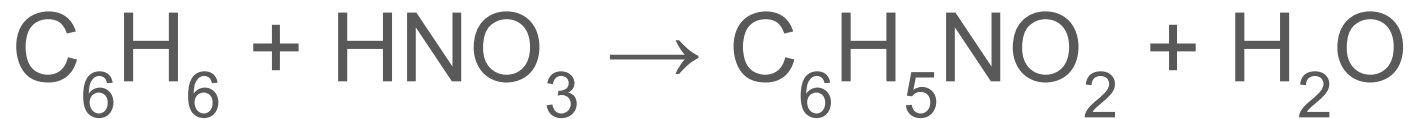
How is the H_2SO_4 catalyst regenerated in the nitration of benzene?



Draw a mechanism and
write an overall equation for
the nitration of benzene



Draw a mechanism and write an overall equation for the nitration of benzene



What are the uses of nitrated arenes?



What are the uses of nitrated arenes?

Production of explosives e.g. TNT

(1-methyl-2,4,6-trinitrobenzene) - releases lots of heat and gas on explosion.

To make aromatic amines that are used for industrial dyes



How do substituents with a positive inductive effect (e.g. alkyl groups) affect further substitution?



How do substituents with a positive inductive effect (e.g. alkyl groups) affect further substitution?

They release electrons into the delocalised electron ring, increasing the electron density and making further substitution reactions more likely/quick.

Direct substituents to the 2,4,6 positions



How do substituents with a negative inductive effect (e.g. NH_2) affect further substitution?



How do substituents with a negative inductive effect (e.g. NH_2) affect further substitution?

Remove electrons from the delocalised electron ring, decreasing the electron density and making further substitution reactions less likely/quick.

Direct substituents to 3,5 positions



What type of catalyst is used for a Friedel-Crafts reaction?



What type of catalyst is used for a Friedel-Crafts reaction?

A halogen carrier (e.g. AlCl_3)



Write an equation to form an electrophile that could be used to acylate benzene, starting with AlCl_3 and RCOCl



Write an equation to form an electrophile that could be used to acylate benzene, starting with AlCl_3 and RCOCl



RCO^+ can attack benzene



What is happening when
 AlCl_4^- is formed in terms of
electrons?



What is happening when AlCl_4^- is formed in terms of electrons?

The lone pair of electrons on the chlorine atom is forming a coordinate bond to Al



How is the AlCl_3 catalyst reformed?



How is the AlCl_3 catalyst reformed?



How could you use a
Friedel-Crafts mechanism to
add a methyl group to a
benzene ring?



How could you use a Friedel-Crafts mechanism to add a methyl group to a benzene ring?

Use a halogenoalkane and AlCl_3 to create an electrophile that can attack benzene

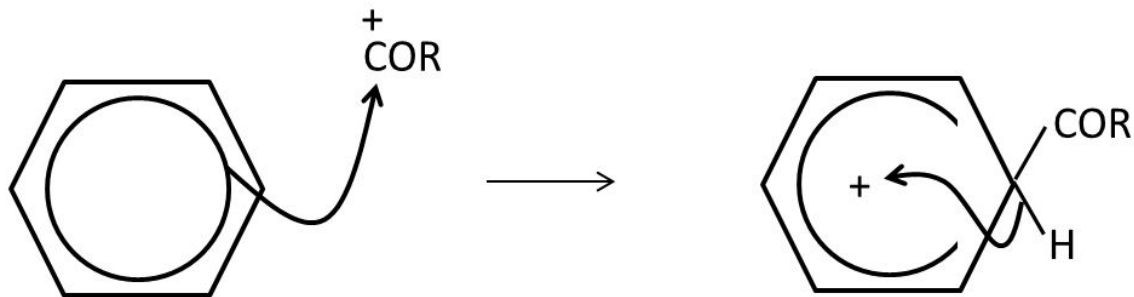


Draw the mechanism for the
acylation of benzene from
 RCO^+ .





Draw the mechanism for the acylation of benzene from RCO^+ .



If you are considering cyclic compounds, what might happen if two double bonds are next to each other?



If you are considering cyclic compounds, what might happen if two double bonds are next to each other?

C=C bonds are in close proximity, so electrons in pi cloud/p orbitals can partially delocalise and move between the two C=C double bonds



What effect would electrons in p orbitals moving between the two C=C double bonds have on the stability of the molecule and its enthalpy of hydrogenation?

What effect would electrons in p orbitals moving between the two C=C double bonds have on the stability of the molecule and its enthalpy of hydrogenation?

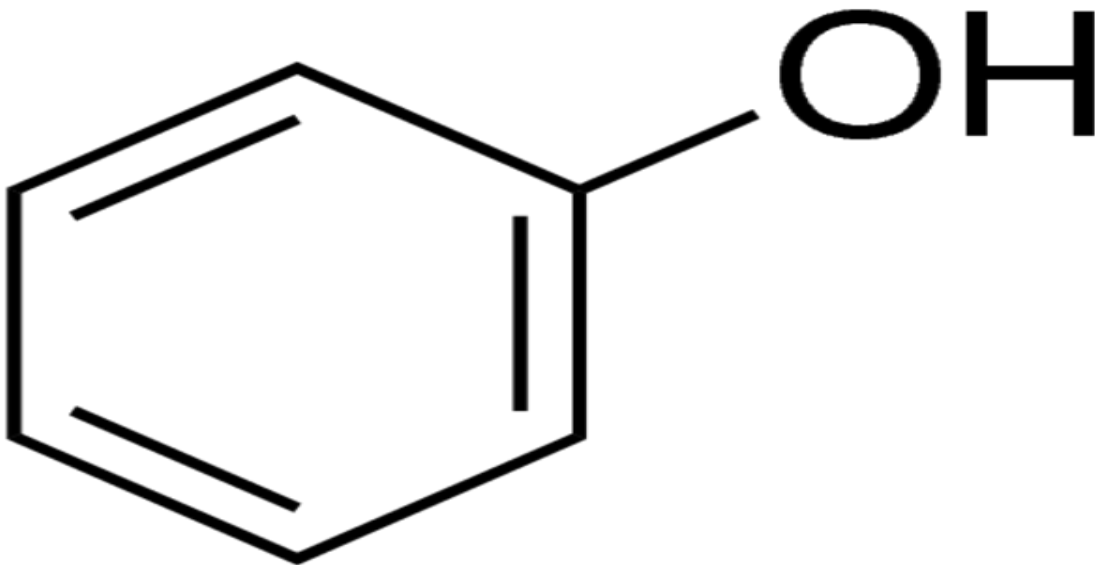
Makes the molecule more stable; makes enthalpy of hydrogenation more positive



What is the structure of phenol?



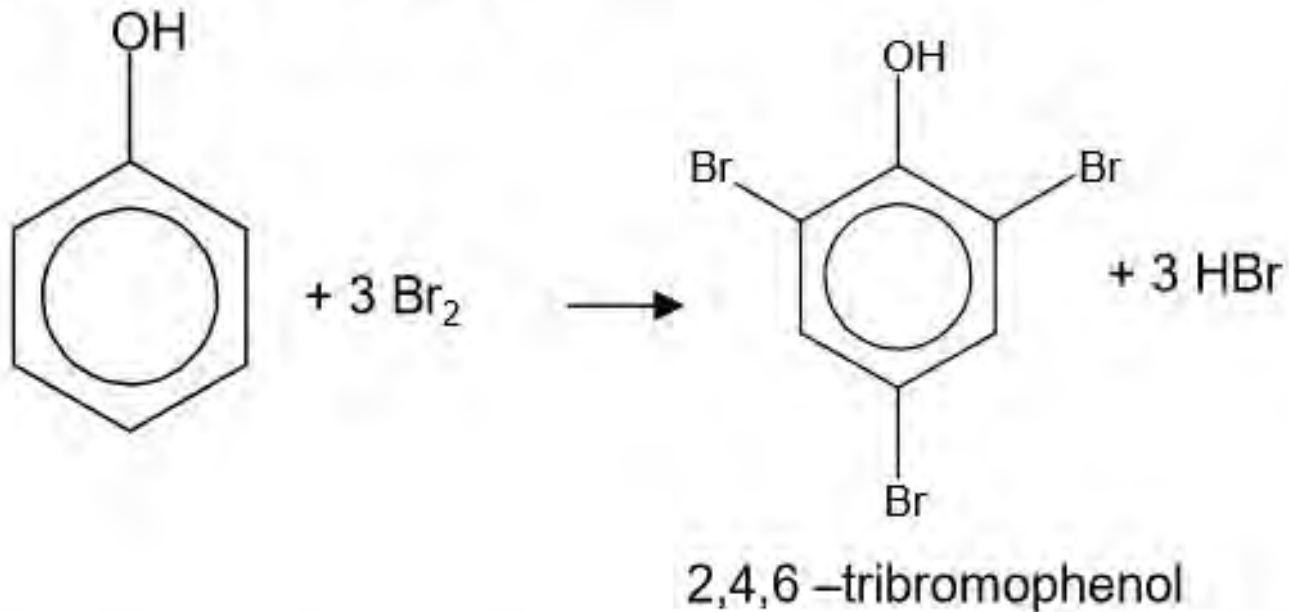
What is the structure of phenol?



Write the equation of the reaction between phenol and bromine water



Write the equation of the reaction between phenol and bromine water



What are the reasons for the relative ease of bromination of phenol, compared to benzene?



What are the reasons for the relative ease of bromination of phenol, compared to benzene?

In a phenol the lone pair of electrons on the oxygen is partially delocalised into the ring and therefore activates the ring and increases electron density. Therefore electrophiles are more attracted to phenol



Why can phenols react with sodium hydroxide but not sodium carbonate?



What are the reasons for the relative ease of bromination of phenol, compared to benzene?

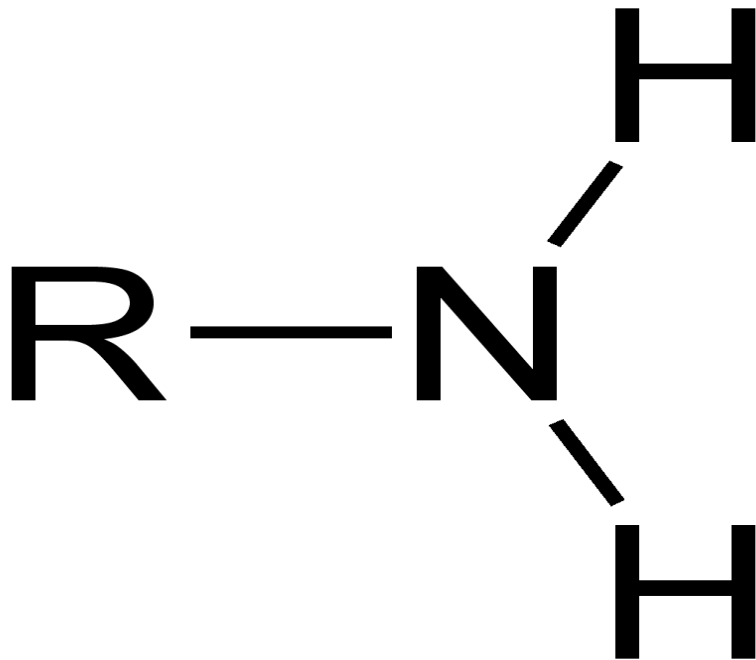
Phenols are very weakly acidic even weaker acids than carboxylic acids. Only carboxylic acids will react with sodium carbonate as a phenol is not strong enough an acid to react.



What is the amine functional group?



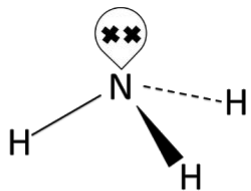
What is the amine functional group?



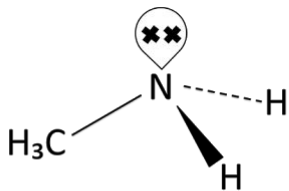
Draw the structures of
primary, secondary and
tertiary amines and a
quaternary ammonium ion



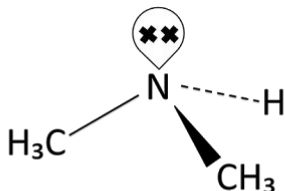
Draw the structures of primary, secondary and tertiary amines and a quaternary ammonium ion.



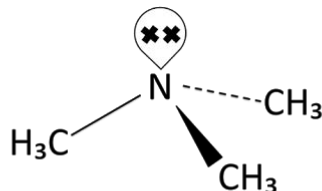
0 carbons
 Ammonia
 (unique)



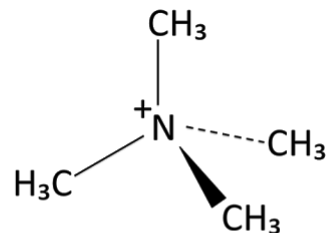
1 carbon
 Primary (1°)
 amine



2 carbons
 Secondary (2°)
 amine



3 carbons
 Tertiary (3°)
 amine



4 carbons
 Quaternary (4°)
 ammonium ion



How do you name amines?



How do you name amines?

-amine or amino-



Why are amines so reactive?



Why are amines so reactive?

The lone pair of electrons on the Nitrogen - due to polar N-H bond



What shape are amines
around the N? Bond angle?



What shape are amines around the N? Bond angle?

Trigonal pyramidal, 107° due to lone pair on N



What kind of intermolecular forces do they have? Why?



What kind of intermolecular forces do they have?

Why?

Hydrogen bonding due to polar N-H bond and lone pair of electrons on N atom.



Do amines have intermolecular forces which are stronger than or weaker than alcohols? Why?



Do amines have intermolecular forces which are stronger than or weaker than alcohols? Why?

Weaker, as N has a lower electronegativity than O → weaker hydrogen bonding



Which primary amines are soluble in water/alcohols?
Why?



Which primary amines are soluble in water/alcohols?
Why?

Up to 4 carbon atoms, as they can hydrogen bond to water molecules. After this, non-polarity of hydrocarbon chain makes them insoluble



What kind of solvents are most other amines soluble in?



What kind of solvents are most other amines soluble in?

Less or non-polar solvents



Solubility of phenylamine?

Why?



Solubility of phenylamine? Why?

Not very soluble, due to the non-polarity of the benzene ring - C_6H_5 cannot form hydrogen bonds



How can/when do amines act as bases?



How can/when do amines act as bases?

When they bond with a H^+ ion



How can/when do amines act as nucleophiles?



How can/when do amines act as nucleophiles?

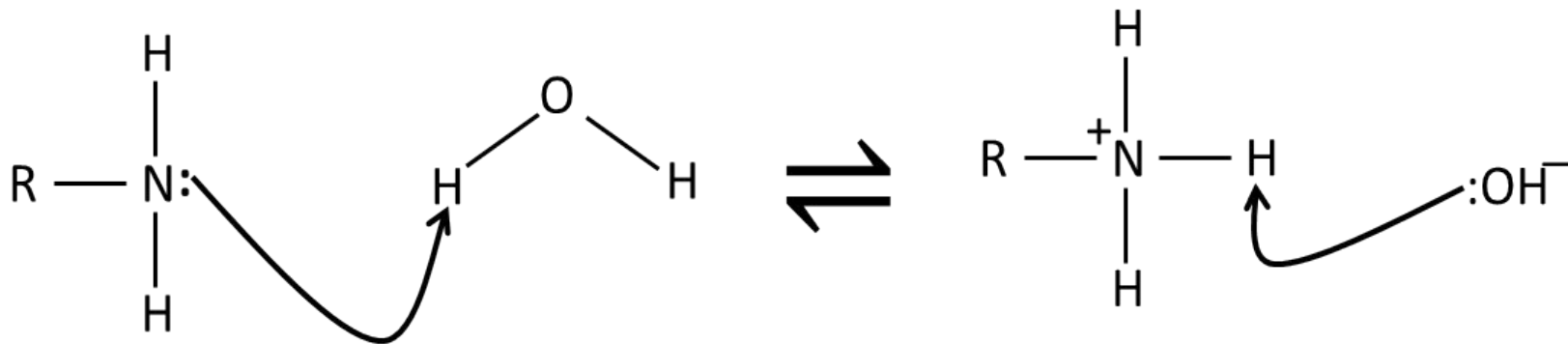
When they bond with an electron-deficient C atom (donate lone pair from N)



Draw a mechanism for the
basic action of an amine
with water



Draw a mechanism for the basic action of an amine with water



What is the product from the basic action of an amine with water?



What is the product from the basic action of an amine with water?

RNH_3^+ - ammonium ion, which forms a salt with an anion



How could you regenerate the soluble amine from the ammonium salt?



How could you regenerate the soluble amine from the ammonium salt?

Add a strong base (NaOH) → removes H^+ ions from ammonium ion



In order to be the strongest base, what must a particular amine have (out of a set of amines)?



In order to be the strongest base, what must a particular amine have (out of a set of amines)?

Greatest electron density around the N atom, making it a better electron pair donor (attracts protons more)



Out of ammonia, primary aliphatic and primary aromatic amines what is the strongest base



Which type of amine is the strongest base?

Primary aliphatic amines are the strongest base and aromatic amines are the weakest. The aromatic amines are the weakest base because the lone pair on nitrogen is partially delocalised into the ring and therefore decreases the attraction of H^+ ion. Primary aliphatic amines are stronger bases than ammonia as the alkyl groups are electron releasing and push electrons towards the nitrogen atom and so make it a stronger base.



What does positive/negative inductive effect mean?



What does positive/negative inductive effect mean?

Positive inductive effect = donate electrons,
increase density around N

Negative means remove electrons, decrease
density around N



What effect do alkyl groups have (on electron density and base strength)?



What effect do alkyl groups have (on electron density and base strength)?

Positive inductive effect - increase electron density around N → stronger base



What effect do acyl groups
have (on electron density
and base strength)?



What effect do aryl groups have (on electron density and base strength)?

Negative inductive effect - decrease electron density around N → weaker base



Why are 3^o amines never
good bases?



Why are 3^o amines never good bases?

They are insoluble in water



Place these in order of base strength (in general): NH_3 ,
 1° amine, 2° amine,
phenylamine



Place these in order of base strength (in general):
 NH_3 , 1° amine, 2° amine, phenylamine

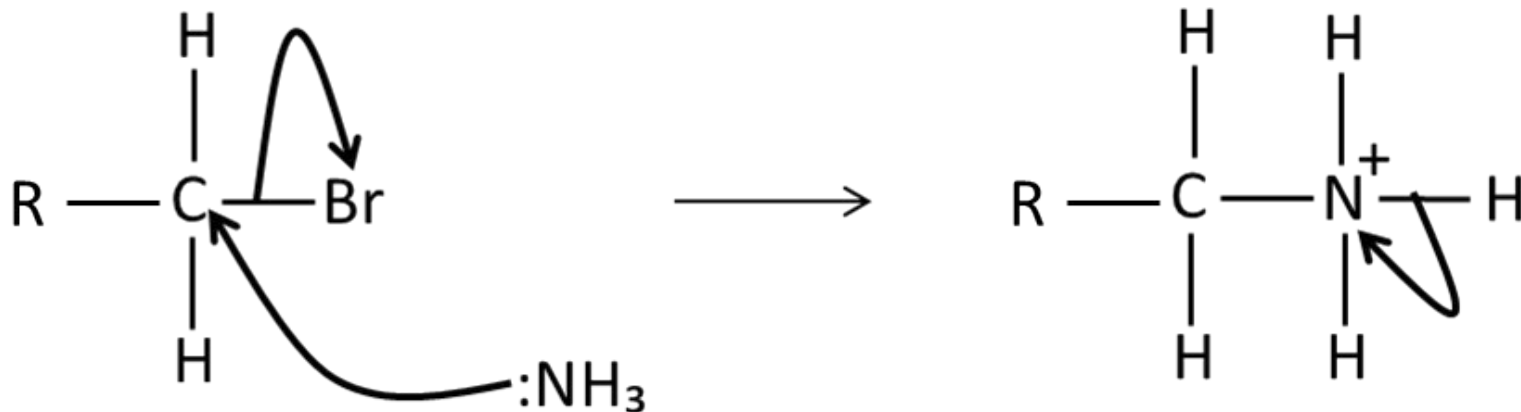
2° amine > 1° amine > NH_3 > phenylamine



Draw a mechanism for the nucleophilic substitution of NH_3 with RCH_2Br to form primary amines



Draw a mechanism for the nucleophilic substitution of NH_3 with RCH_2Br to form primary amines



How can primary amines
then form 2^o, 3^o amines and
4^o ammonium ions?



How can primary amines then form 2°, 3° amines and 4° ammonium ions?

Multiple substitutions; primary amine is a nucleophile that attacks the original haloalkane etc



What are the problems with this method?



What are the problems with this method?

Not efficient as low yield of 1° amine due to multiple substitutions



How would you maximise
the yield of the primary
amine?



How would you maximise the yield of the primary amine?

Use excess ammonia



How do you get from a nitrile to a primary amine?
(name of reaction type and reagents/catalysts)



How do you get from a nitrile to a primary amine?
(name of reaction type and reagents/catalysts)

Reduction using Nickel / Hydrogen catalyst



Why is this a purer method of synthesising amines?



Why is this a purer method of synthesising amines?

Only the primary amine can be formed



How do you form an ammonium chloride salt from nitrobenzene? What conditions are needed?



How do you form an ammonium chloride salt from nitrobenzene? What conditions are needed?

Reduce the nitrile using Tin / HCl → forms an ammonium salt with Cl⁻ ions

Room temperature



Equation for the reaction of
nitrobenzene \rightarrow
phenylamine?



Equation for the reaction of nitrobenzene →
phenylamine?



What mechanism is used for forming amides from acyl chlorides and amines?



What mechanism is used for forming amides from acyl chlorides and amines?

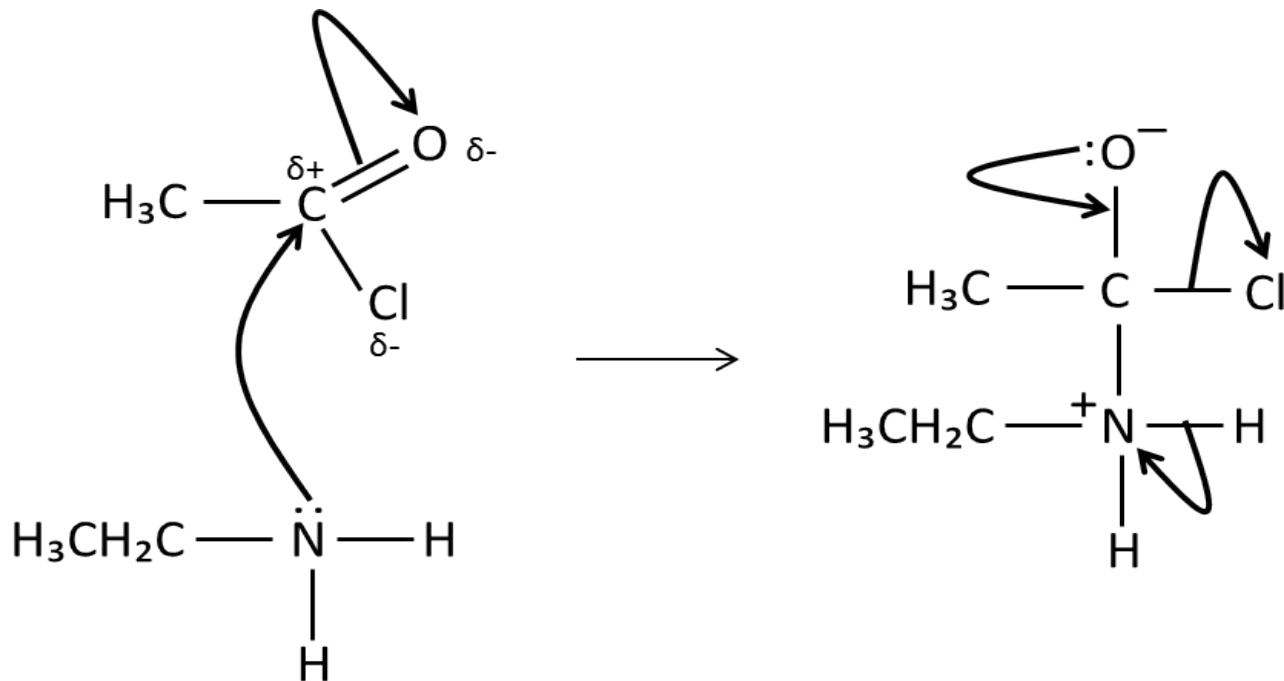
Nucleophilic addition/elimination



Draw a mechanism for the reaction of ethanoyl chloride with ethanamine.



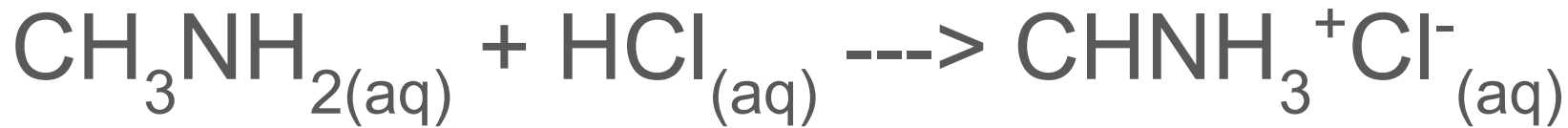
Draw a mechanism for the reaction of ethanoyl chloride with ethanamine.



Write an equation showing
the reaction between
methylamine with HCl



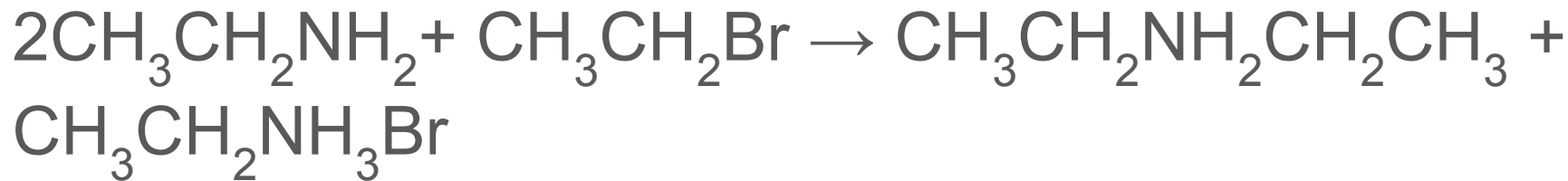
Write an equation showing the reaction between methylamine with HCl



Write an equation showing
the reaction between
ethylamine and
bromoethane



Write an equation showing the reaction between ethylamine and bromoethane



Write an equation illustrating
the reaction between
ethylamine and copper (II)
ions



Write an equation illustrating the reaction between ethylamine and copper (II) ions



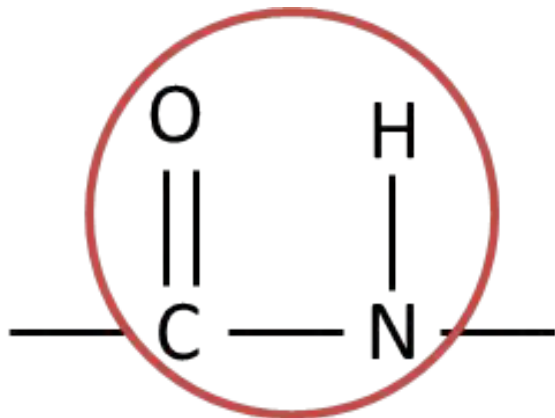
How do you prepare amines from acyl chlorides?



What is the linkage in a polyamide?



What is the linkage in a polyamide?



The peptide linkage



Which molecule is eliminated when a polyamide is formed via condensation reaction?



Which molecule is eliminated when a polyamide is formed?



What are the two monomers
used to form a polyamide
(generic names and
structures)?



What are the two monomers used to form a polyamide (generic names and structures)?

Diamine and dicarboxylic acid



Examples of polyamides?



Examples of polyamides?

Nylon, Kevlar

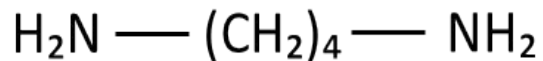


Which monomers is
Nylon-6,6 made from?



Which monomers is Nylon-6,6 made from?

1,6-diaminohexane



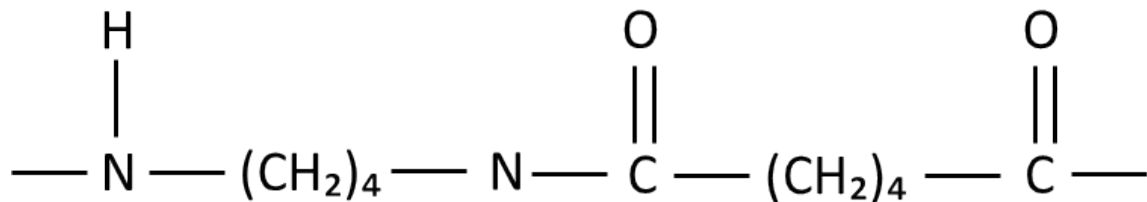
Hexanedioic acid



Draw the repeating unit of Nylon-6,6.



Draw the repeating unit of Nylon-6,6.



How do you prepare amines from acyl chlorides?

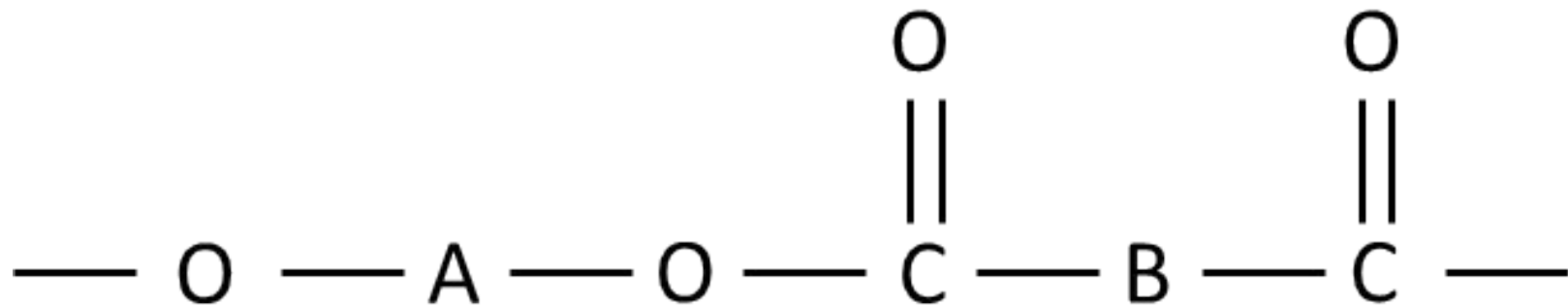
Use a primary amine and the condition is room temperature



Draw a generic repeating unit for a polyester



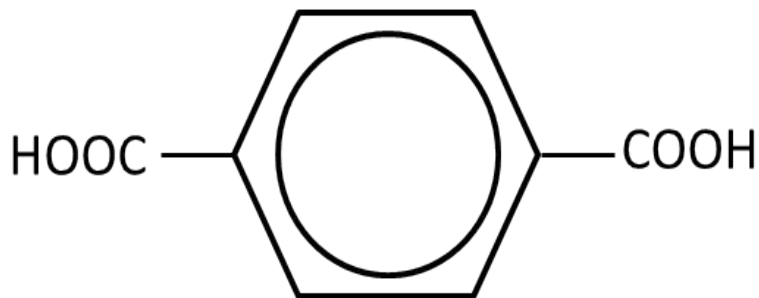
Draw a generic repeating unit for a polyester



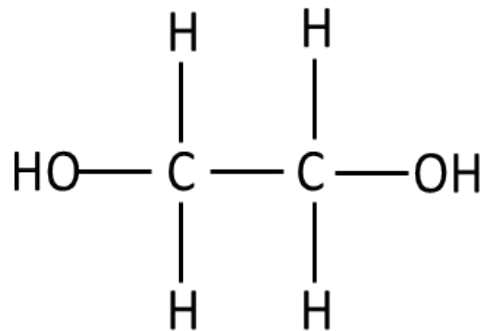
Which monomers is Terylene made from?



Which monomers is Terylene made from?



Benzene-1,4-dicarboxylic acid



Ethane-1,2-diol

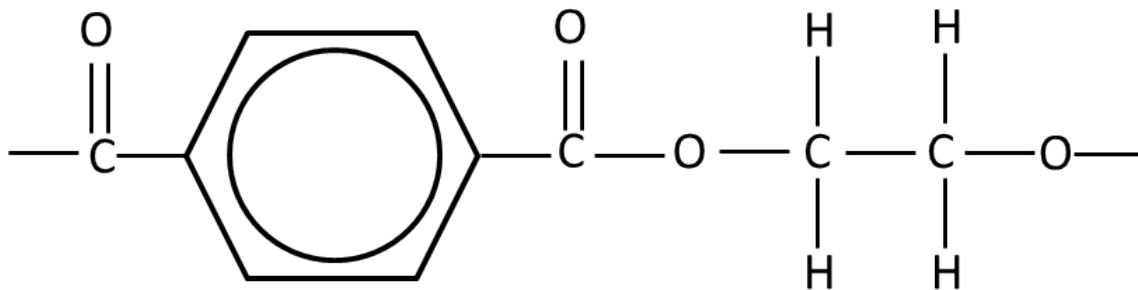


Draw the repeating unit of Terylene





Draw the repeating unit of Terylene



What are the two functional groups of amino acids?



What are the two functional groups of amino acids?

NH_2 and COOH (amine and carboxylic acid)



How many naturally occurring amino acids are there in the body?



How many naturally occurring amino acids are there in the body?

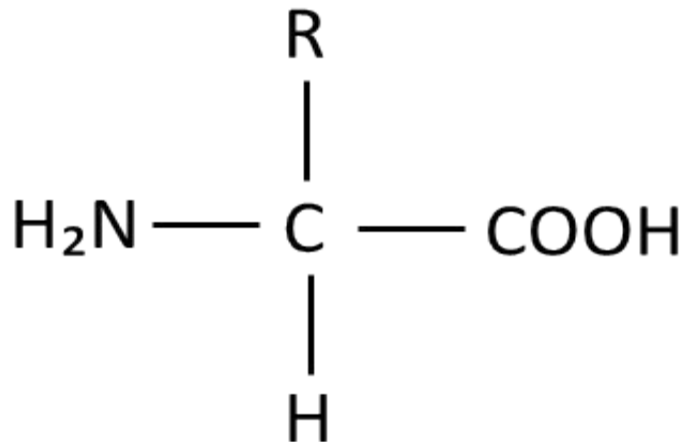
20



Draw a general formula for α -amino acids



Draw a general formula for α -amino acids



Are α -amino acids chiral? Why?



Are α -amino acids chiral? Why?

Yes, one carbon has 4 different substituents.

Except glycine, where $R = H$.



Which enantiomer do
 α -amino acids exist as in
nature?



Which enantiomer do α -amino acids exist as in nature?

(-) enantiomer



How can amino acids be synthesised industrially?



How can amino acids be synthesised industrially?

$\text{RCHO} + \text{NH}_4\text{CN} \rightarrow \text{RCH}(\text{NH}_2)\text{CN}$ via nucleophilic addition.

$\text{RCH}(\text{NH}_2)\text{CN} + \text{HCl} + 2\text{H}_2\text{O} \rightarrow \text{RCH}(\text{NH}_2)\text{COOH} + \text{NH}_4\text{Cl}$

(hydrolysis, HCl is dilute) Need to reflux the reaction mixture



Is the product from amino acids being synthesised naturally optically active?
Why?



Is the product from amino acids being synthesised naturally optically active? Why?

No, a racemic mixture is formed as the CN^- ion can attack from above or below the planar $\text{C}=\text{O}$ bond with equal likelihood. An equal amount of each enantiomer is formed, so no net effect on plane polarised light.



In what form do amino acids exist as solids? What consequences does this have?



In what form do amino acids exist as solids? What consequences does this have?

Zwitterions (ionic lattice) - high melting and boiling points



What colour solids are most
zwitterions at room
temperature?



What colour solids are most zwitterions at room temperature?

White solids



Do zwitterions dissolve in
water? Non-polar solvents?
Why?



Do zwitterions dissolve in water? Non-polar solvents? Why?

Yes, but not in non-polar solvents. Due to ionic nature/polar bonds.



Define a zwitterion



Define a zwitterion

Ions which have both a permanent positive and negative charge, but are neutral overall.



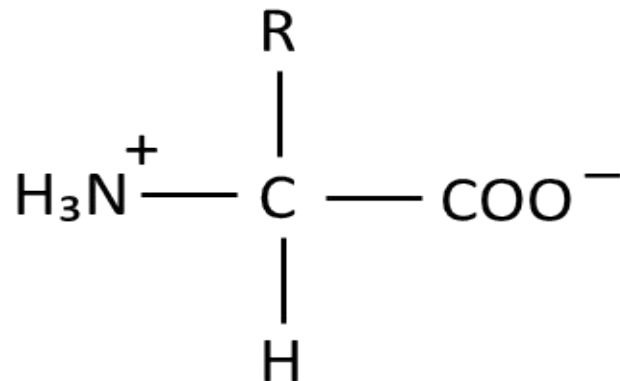
How do zwitterions occur in amino acids? Draw a general structure of one



How do zwitterions occur in amino acids? Draw a general structure of one

COOH is deprotonated \rightarrow COO⁻

NH₂ is protonated \rightarrow NH₃⁺

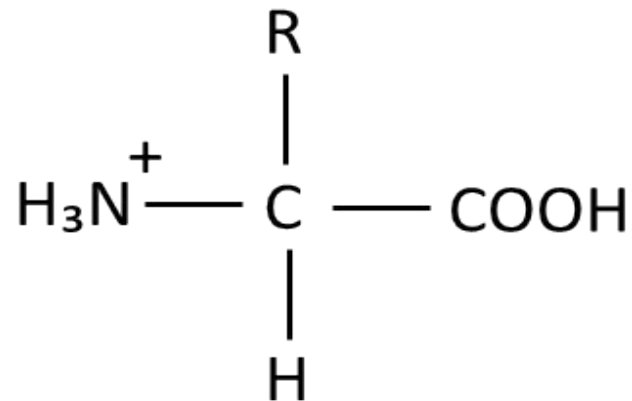


What happens to amino acids in acidic conditions?
Draw this.



What happens to amino acids in acidic conditions?
Draw this.

Gains a proton on NH_2 group

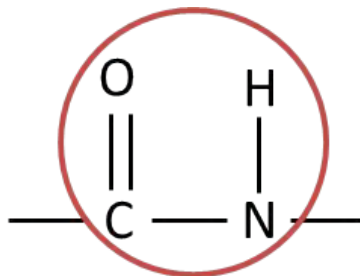


What happens to amino acids in alkaline conditions?
Draw this.



What is the peptide linkage?

-CONH-



The peptide linkage

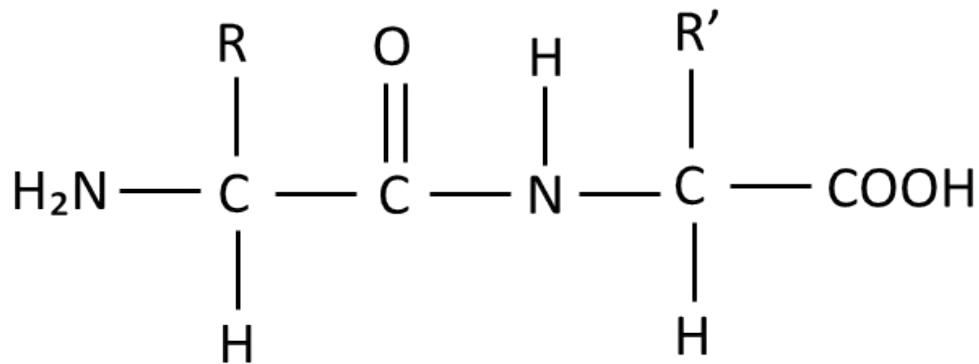


What is a dipeptide? Draw a general one for amino acids.



What is a dipeptide? Draw a general one for amino acids.

Two amino acids bonded together (a dimer)



What name is given to
chains of amino acids up to
50 amino acids?



What name is given to chains of amino acids up to
50 amino acids?

Polypeptides



What name is given to chains of amino acids with more than 50?



What name is given to chains of amino acids with more than 50?

Proteins



What are polypeptides and proteins found in?



What are polypeptides and proteins found in?

Enzymes

Wool

Hair

Muscles



What is the process called by which polypeptides or proteins can be broken down into their constituent amino acids?



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hydrolysis



What conditions are needed for hydrolysis to occur?



What conditions are needed for hydrolysis to occur?

6 mol dm⁻³ HCl, reflux for 24 hours



What is a TLC plate made of?



What is a TLC plate made of?

Plastic sheet coated with silica, SiO_2 . This is the stationary phase. (The solvent is the mobile phase)



Describe how you would carry out Thin Layer Chromatography



Describe how you would carry out Thin Layer Chromatography

Spot the samples onto a pencil line a few cm above the base of the TLC plate.

Place this in a beaker or tank, with solvent level below the pencil line. Ensure there is a lid on the beaker to keep the inside saturated with solvent vapour.

Wait until the solvent front is almost at the top of the TLC plate; then remove from the beaker and analyse.



Why does TLC separate
amino acids (or other
molecules)?



Why does TLC separate amino acids (or other molecules)?

Solvent carries amino acids up the TLC plate. The rate of movement depends on the balance between that amino acid's affinity for the solvent (solubility in it) and affinity for the stationary phase (attraction to the silicon with hydrogen bonding).



What do you often have to do to enable the amino acids to be seen on the chromatogram?



What do you often have to do to enable the amino acids to be seen on the chromatogram?

Spray with ninhydrin (amino acids are colourless, ninhydrin turns their spots purple)

Or shine UV light on them



What would you observe in
a melting point
determination if the sample
was not pure?



What would you observe in a melting point determination if the sample was not pure?

Sample melts over a large range (more than 3°C).

Sample's melting point is below the accepted value due to impurities disrupting structure



Why might the melting point appear different to the true value?



Why might the melting point appear different to the true value?

Temperature of the material in the machine might be different to the temperature shown on the thermometer - apparatus error.



When purifying by
recrystallisation, why is the
minimum volume of hot
solvent used?



When purifying by recrystallisation, why is the minimum volume of hot solvent used?

So that a saturated solution is created, so that as many crystals will fall out of solution as possible when it is cooled



Why is the solution filtered hot when purifying by recrystallisation?



Why is the solution filtered hot when purifying by recrystallisation?

To remove insoluble impurities and ensure that the crystals do not form in the filter paper



Why is the solution cooled
in an ice bath when
purifying by
recrystallisation?



Why is the solution cooled in an ice bath when purifying by recrystallisation?

To ensure that as many crystals as possible fall out of solution - yield is higher



Why are the crystals washed with cold water when purifying by recrystallisation?



Why are the crystals washed with cold water when purifying by recrystallisation?

To remove soluble impurities



How would you separate the crystals from the reaction mixture when purifying by recrystallisation?



How would you separate the crystals from the reaction mixture when purifying by recrystallisation?

Filter under reduced pressure using a Buchner funnel



Why might percentage yield be below 100% (practical reasons)?



Why might percentage yield be below 100% (practical reasons)?

Product is lost during filtration, drying and weighing - spills, not all transferred from one piece of apparatus to the other

Product is left dissolved in the solution - some does not crystallise. Some left on filter paper. Sample still wet



In a distillation setup, why is it necessary to have a continuous water flow around the condenser?



In a distillation setup, why is it necessary to have a continuous water flow around the condenser?

So that the water remains cool in order for the mixture to be distilled



Describe a method that can be used to separate immiscible liquids



Describe a method that can be used to separate immiscible liquids

- Pour the mixture into a separating funnel and some distilled water
- Add the stopper and invert the flask to mix the mixture
- Equalise the pressure by opening the stopper as required
- Continue shaking until there is no 'whistle' sound
- To collect the water in the lower layer, open the stopper and place a beaker under the spout
- Use another beaker to collect the desired organic layer
- Shake the liquid with some drying agent



Name two drying agents



Name two drying agents

Magnesium sulphate

Calcium chloride



How are drying agents used?



How are drying agents used?

- Add a selected drying agent to the organic product
- If the drying agent forms clumps add some more until they are moving freely
- Use gravity filtration to collect the dry product.
- Filtrate is the product



What does re-distillation mean?



What does re-distillation mean?

When a liquid is purified by using multiple distillations



How to prepare Grignard Reagent



How to prepare Grignard Reagent

A halogenoalkane is dissolved in dry ether and reacted with magnesium.



What are the two ways to increase the length of the carbon chain in a molecule by the use of magnesium to form Grignard reagents



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React Grignard reagent:

with carbon dioxide

with carbonyl compounds in dry ether

