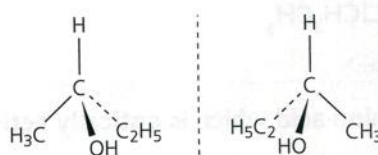


# Organic chemistry

## Topic 7 Optical isomerism

Stereoisomers are molecules that have the same structural formula but a different arrangement of atoms in space. Optical isomers (enantiomers) are stereoisomers that occur as a result of chirality in molecules. They exist as non-superimposable mirror images and differ in their effect on plane polarised light. An asymmetric carbon atom is chiral and has four different atoms or groups attached.

When drawing optical isomers, identify the chiral centre, draw the three-dimensional tetrahedral structure based on the chiral centre and insert the four different groups. Then draw a dotted line to represent a mirror, and draw the second isomer by reflecting the isomer in an imaginary mirror. The optical isomers of butan-2-ol are shown here.



An optically active substance is one that can rotate the plane of plane polarised light. Plane polarised light is light in which all the waves vibrate in the same plane. Optical isomers each *rotate the plane of plane polarised light in opposite directions* and hence they are optically active. Mixing equal amounts of the same concentration of two enantiomers gives an *optically inactive mixture*, which has no effect on plane polarised light because the two opposite effects cancel out. This mixture of equal amounts of each enantiomer is called a racemic mixture or racemate.

**1** Which one of the following molecules exhibits optical isomerism? (AO3)

1 mark

- A  $\text{CH}_3\text{CHBrCH}_3$
- B  $\text{CH}_3\text{CH}_2\text{COCCH}_3$
- C  $\text{CH}_3\text{CH}_2\text{CHClCH}_3$
- D  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$

**2** Which one of the following is the total number of isomers, both structural and stereoisomers, which are possible for the formula  $\text{C}_4\text{H}_{10}\text{O}$ ? (AO3)

1 mark

- A 3 or less
- B 4
- C 5
- D 6 or more

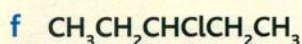
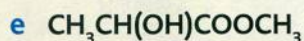
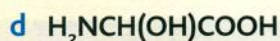
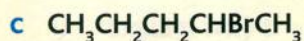
**3** State if the following structures have optical isomers. (AO3)

6 marks

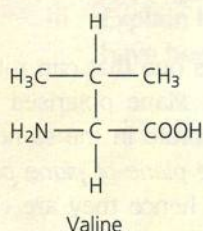
a  $\text{CH}_3\text{CHClCH}_2\text{CH}_3$

b  $\text{CH}_3\text{CH}_2\text{OH}$





- 4 Valine is an amino acid which is optically active.



- a Explain the term optically active. (AO1)

1 mark

- b Draw the three-dimensional structures for the two optical isomers of valine. (AO2)

2 marks

- c State how a racemic mixture of valine is prepared and state and explain its effect on plane polarised light. (AO1)

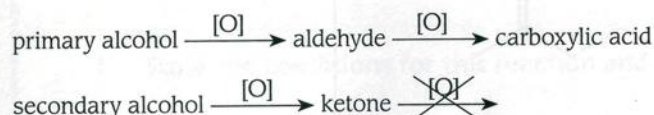
4 marks



# Topic 8 Aldehydes and ketones

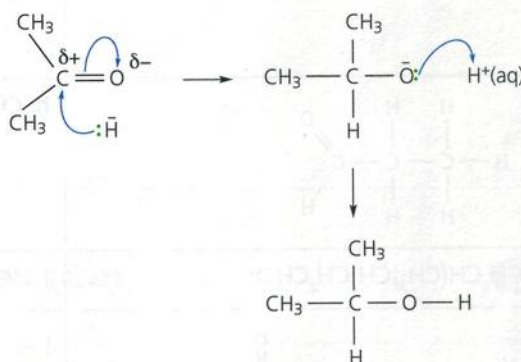
Aldehydes and ketones both contain the carbonyl group  $C=O$  which is polar. Aldehydes are named *-anal* and the carbonyl group is always at the end of the chain, so a positional number is not needed. Ketones are named *-anone*. The carbonyl group can be at any position on the chain, except for the end.

Aldehydes and ketones are the products of the oxidation of alcohols. Aldehydes can be oxidised into carboxylic acids, on warming with the oxidising agent  $[O]$  acidified potassium dichromate(vi).

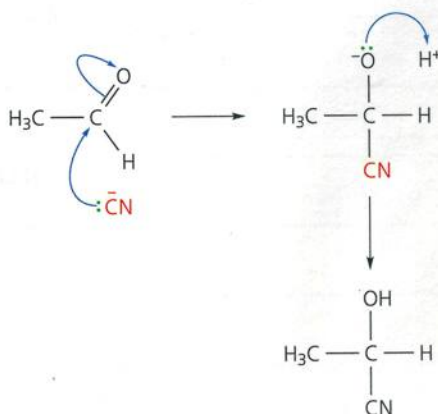


Aldehydes are oxidised to carboxylic acids by warming with Tollens' reagent, which changes from a colourless solution to a silver mirror. Ketones are not oxidised. Fehling's solution can also oxidise aldehydes: the blue solution changes to a red precipitate. These are tests for aldehydes.

Aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols by sodium tetrahydridoborate(III) ( $NaBH_4$ ) in a nucleophilic addition reaction. The  $BH_4^-$  ion in  $NaBH_4$  is a source of the nucleophile, hydride ions ( $H^-$ ).



Aldehydes and ketones react with  $KCN$  followed by dilute acid in a nucleophilic addition reaction to form a hydroxynitrile. The cyanide ion is the nucleophile. The mechanism for ethanal and  $KCN$  and dilute acid is shown below.



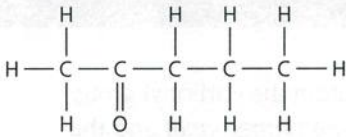
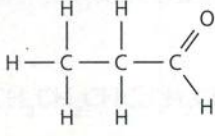
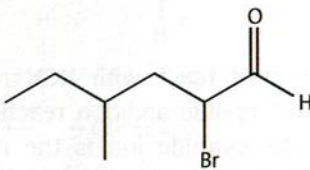
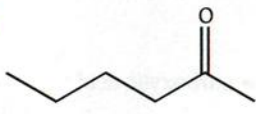
All aldehydes produce a racemate in this reaction. Unsymmetrical ketones (for example,  $CH_3COCH_2CH_3$ ) will produce a racemate. Symmetrical ketones (for example,  $CH_3COCH_3$ ) produce a product which does not have an asymmetric carbon and is optically inactive.

## 1 Name the following organic compounds. (AO2)

12 marks

Compound	Compound
<b>a</b> $  \begin{array}{c}  \text{H} & & \text{H} \\    & &   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\    &    &   \\  \text{H} & \text{O} & \text{H}  \end{array}  $	<b>b</b> $  \begin{array}{c}  \text{H} & & \text{O} \\    & &    \\  \text{H}-\text{C}-\text{C}-\text{H} \\    & & \\  \text{H} & &   \end{array}  $
<b>c</b> $  \begin{array}{c}  \text{H} & \text{H} & & \text{H} & \text{H} \\    &   & &   &   \\  \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\    &   &    &   &   \\  \text{H} & \text{H} & \text{O} & \text{H} & \text{H}  \end{array}  $	<b>d</b> $CH_3CH_2CH_2CHO$



Compound	Compound
e $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$	f 
g 	h $\text{CH}_3\text{CH}(\text{CH}_3)\text{CHO}$
i $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CHO}$	j $\text{HCHO}$
k 	l 

- a .....
- b .....
- c .....
- d .....
- e .....
- f .....
- g .....
- h .....
- i .....
- j .....
- k .....
- l .....

2 Use the table in question 1 to answer the following.

- a Choose three sets of substances which are functional group isomers. (AO3)

3 marks

.....

.....

.....

- b What is the molecular formula of k? (AO2)

1 mark

.....

.....



- 3 Which one of the following describes the mechanism for the reaction of potassium cyanide with propanone? (AO1)

1 mark

- A electrophilic addition  
B electrophilic substitution  
C nucleophilic addition  
D nucleophilic substitution

- 4 Propanal can be reduced using  $\text{NaBH}_4$ .

- a Write an equation for the reduction of propanal. (AO2)

1 mark

- b State the conditions for this reaction and name the organic product. (AO3)

2 marks

- c Name the nucleophile in this reaction. (AO1)

1 mark

- d Outline the mechanism for the reduction. (AO1)

3 marks

- e Draw the structure of a ketone which is an isomer of propanal. (AO1)

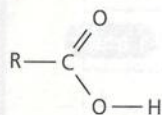
1 mark



# Topic 9 Carboxylic acids and derivatives

## Carboxylic acids and esters

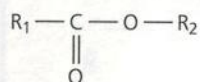
Carboxylic acids have the structure shown below, where R is an alkyl group:



They are named -anoic acid. The carboxyl carbon in the COOH functional group is always carbon number 1.

Carboxylic acids are *weak acids* because they are partially dissociated in solution. Carboxylic acids take part in typical acid reactions — with carbonates to form carbon dioxide, water and a salt, with metals to form hydrogen and a salt and with bases to form a salt and water. Despite being weak acids, carboxylic acids are stronger than carbonic acid and release carbon dioxide, which makes colourless limewater cloudy, when reacted with carbonates. This reaction is used to test for carboxylic acids.

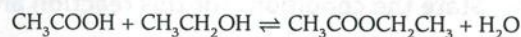
Esters have the general structure:



R<sub>1</sub> is from the acid and R<sub>2</sub> is from the alcohol. The functional group of an ester is the -COO- group. When

naming, the alcohol provides the *alkyl* part of the name and the carboxylic acid provides the *carboxylate* part of the name. For example, the ester made from methanol and propanoic acid is methyl propanoate, CH<sub>3</sub>CH<sub>2</sub>COOCH<sub>3</sub>. Esters are used as plasticisers, which are additives mixed into polymers to improve their flexibility, as solvents in paints, in perfumes and in food flavourings.

Carboxylic acids react when heated with alcohols, in the presence of a concentrated sulfuric acid catalyst to produce esters, in an equilibrium reaction.



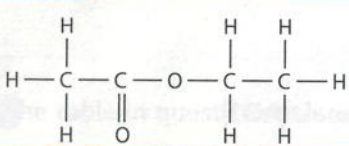
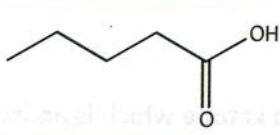
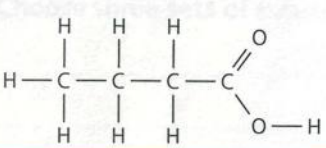
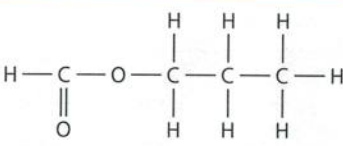
Esters can be hydrolysed in acid conditions to produce alcohols and carboxylic acids, and in alkaline conditions to produce alcohols and carboxylic acid salts. The reaction in alkaline solution is quicker. In order to liberate the free acid from its salt in alkaline hydrolysis, a dilute mineral acid such as dilute hydrochloric acid should be added.

Vegetable oil and animal fats are esters of propane-1,2,3-triol (glycerol) and a long-chain fatty acid, and can be hydrolysed to produce long-chain carboxylic acid salts (soap) and glycerol. This alkaline hydrolysis of fats is called saponification.

Biodiesel is a renewable fuel which consists of a mixture of methyl esters of long-chain carboxylic acids which is produced by heating vegetable oils with methanol in the presence of an acid catalyst.

### 1 Name the following organic compounds. (AO2)

8 marks

Compound	Compound
<b>a</b> 	<b>b</b> 
<b>c</b> 	<b>d</b> CH <sub>2</sub> (OH)CH <sub>2</sub> COOH
<b>e</b> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>3</sub>	<b>f</b> CH <sub>3</sub> CH <sub>2</sub> COOH
<b>g</b> CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<b>h</b> 



a

b

c

d

e

f

g

h

2 Which one of the following organic compounds does not exist? (AO3)

1 mark

A an aldehyde with formula  $C_2H_4O$

B an alkene with formula  $C_4H_8$

C an ester with formula  $C_3H_6O_2$

D a ketone with formula  $C_2H_4O$

3 Write equations for the reaction of:

a propanoic acid and magnesium (AO2)

1 mark

b ethanoic acid and sodium carbonate (AO2)

1 mark

c butanoic acid and sodium hydroxide (AO2)

1 mark

d ethanoic acid and propanol (AO2)

1 mark

e propanoic acid and methanol (AO2)

1 mark

- 4 a Draw the structure and give the IUPAC name for glycerol. (AO1)

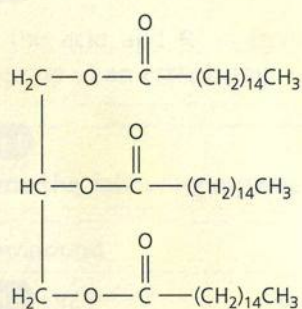
2 marks

- b Write an equation for the reaction of glycerol with three molecules of the stearic acid  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$  to form a fat. (AO2)

2 marks

- c Write an equation for the saponification of the fat A shown below using sodium hydroxide. (AO2)

2 marks



Fat A



- d The fat A can be used to make biodiesel. Suggest the conditions used and write an equation. (AO1/AO2)

4 marks

## Acylation

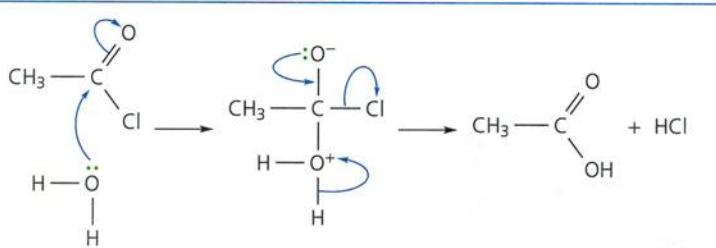
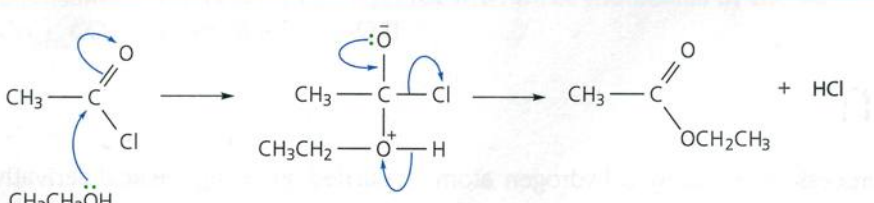
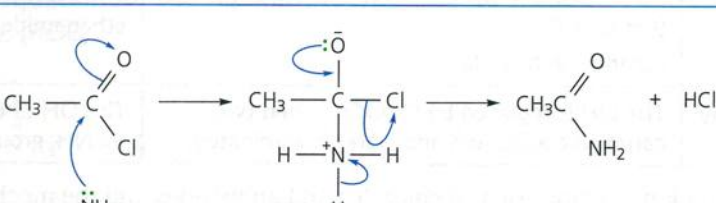
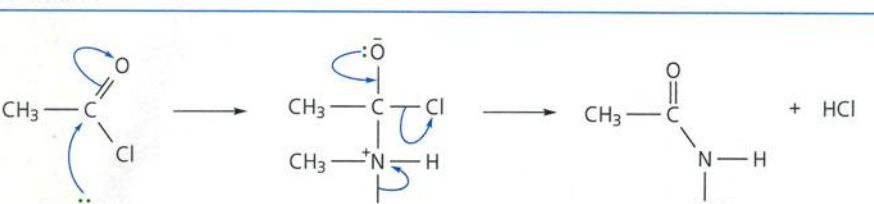
Acylation is the process of replacing a hydrogen atom in certain molecules by an acyl group ( $\text{RCO}-$ ). It can be

carried out using the acid derivatives shown in the table below.

Acyl chloride	Acid anhydride	Amide
$\text{H}_3\text{C}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{Cl} \end{array}$ <p>Ethanoyl chloride</p>	$\text{H}_3\text{C}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O} \end{array} \text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_3 \end{array}$ <p><math>(\text{CH}_3\text{CO})_2\text{O}</math> Ethanoic anhydride</p>	$\text{CH}_3-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{NH}_2 \end{array}$ <p>Ethanamide</p>
The OH of the acid is replaced by a chlorine atom.	The OH is replaced by $\text{OCOCH}_3$ when two carboxylic acids join and water is eliminated.	The OH of the acid is replaced by an $\text{NH}_2$ group.

The nucleophilic addition–elimination reactions of acyl chlorides and anhydrides and the mechanisms that you need to know are shown on page 24.



Reaction	Nucleophile	Products
Acyl chloride	Water	$\text{CH}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HCl}$ Carboxylic acid + HCl
	<b>Mechanism</b> 	
Acid anhydride	Water	$(\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{CH}_3\text{COOH}$ Carboxylic acid
Acyl chloride	Alcohol	$\text{CH}_3\text{COCl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{HCl}$ Ester + HCl
	<b>Mechanism</b> 	
Acid anhydride	Alcohol	$(\text{CH}_3\text{CO})_2\text{O} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{CH}_3\text{COOH}$ Ester + carboxylic acid
Acyl chloride	Ammonia	$\text{CH}_3\text{COCl} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CONH}_2 + \text{NH}_4\text{Cl}$ Amide + HCl
	<b>Mechanism</b> 	
Acid anhydride	Ammonia	$(\text{CH}_3\text{CO})_2\text{O} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CONH}_2 + \text{CH}_3\text{COONH}_4$ Amide + carboxylic acid salt
Acyl chloride	Primary amine	$\text{CH}_3\text{COCl} + 2\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{CONHCH}_3 + \text{CH}_3\text{NH}_3\text{Cl}$ N-substituted amine + HCl
	<b>Mechanism</b> 	
Acid anhydride	Primary amine	$(\text{CH}_3\text{CH}_2\text{CO})_2\text{O} + 2\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CONHCH}_3 + \text{CH}_3\text{CH}_2\text{COONH}_3\text{CH}_3$ N-substituted amide + carboxylic acid



Aspirin is manufactured by acylating 2-hydroxybenzenecarboxylic acid. The *industrial advantages* of using ethanoic anhydride to acylate rather than ethanoyl chloride include:

- It is less corrosive.
- It is less vulnerable to hydrolysis.
- It is less hazardous to use as it gives a less violent reaction.
- It is cheaper than ethanoyl chloride.
- It does not produce corrosive fumes of hydrogen chloride.

Organic solids, such as aspirin, must be produced in as pure a state as possible and are purified by recrystallisation. In *recrystallisation* the impure crystals are dissolved in the *minimum volume of hot solvent*, the solution cooled and crystallised and the crystals filtered using suction filtration. A melting point can be determined by placing some of the solid in a melting point apparatus, heating slowly and recording the temperature at which the solid starts to melt and the temperature at which it finishes melting. Repeat and average the temperatures. Compare the melting point with known values in a data book.

- 1** Which one of the following statements about the formation of an ester from ethanoyl chloride and propan-1-ol is correct? (AO1)

1 mark

- A Concentrated sulfuric acid is required.
- B Heat is required.
- C The ester produced is called ethyl propanoate.
- D The reaction goes to completion.

- 2 a** Name and outline a mechanism for the reaction of  $\text{CH}_3\text{CH}_2\text{COCl}$  with  $\text{CH}_3\text{NH}_2$ . (AO1)

4 marks

- b** Give the name of the product containing an amide linkage that is formed in the reaction in part (a). (AO3)

1 mark



## Exam-style questions

- 1 Which one of the following is the correct systematic name for the compound  $\text{CH}_2\text{BrCOCH}_2\text{CH}_3$ ? 1 mark

A 1-bromobutan-2-one  
B 1-bromobutan-3-one  
C 4-bromobutan-2-one  
D 4-bromobutan-3-one

- 2 Which one of the following compounds is optically active and incapable of reducing Tollens' reagent? 1 mark

A  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$   
B  $\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{COCH}_3$   
C  $\text{CH}_3\text{CHClCH}_2\text{CHO}$   
D  $\text{CH}_3\text{CH}(\text{CH}_3)\text{COCH}_3$

- 3 Which one of the following compound is formed when methanol is added to  $\text{CH}_2\text{CH}_2\text{ClCOCl}$ ? 1 mark

A  $\text{CH}_2\text{OCH}_3\text{COCl}$   
B  $\text{CH}_2\text{CH}_2\text{OCH}_3\text{COCH}_3$   
C  $\text{CH}_2\text{CH}_2\text{ClCO}_2\text{CH}_3$   
D  $\text{CH}_2\text{ClCOCH}_3$

- 4 Palmitic acid,  $\text{C}_{15}\text{H}_{31}\text{COOH}$ , forms a triglyceride when it reacts with glycerol.

a What is the empirical formula for palmitic acid? 1 mark

b Write the equation for the reaction of palmitic acid with glycerol. 3 marks

- 5 Aldehydes contain the carbonyl functional group.

a On the diagram below show the polarity of the carbonyl group. 1 mark





- b** Ethanal reacts with hydrogen cyanide. Write an equation for this reaction and name the organic product.

2 marks

- C** Name and outline the mechanism for the reaction of ethanal with hydrogen cyanide.

4 marks

- d** Ethanal reacts with cold dilute potassium carbonate solution to yield 3-hydroxybutanal,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$  which is optically active.

- i** Draw the three-dimensional structures for the two optical isomers of 3-hydroxybutanal.

**2 marks**

- ii 3-hydroxybutanal may be dehydrated to form but-2-enal. Suggest a structure for but-2-enal.

1 mark



6 An ester may be prepared in the laboratory by the reaction of propanoic acid and methanol.

a Write the equation for the preparation of methyl propanoate.

1 mark

b Concentrated sulfuric acid is added to the reaction mixture. State one function of this acid in the preparation.

1 mark

c Propanoic acid has a boiling point of  $141^{\circ}\text{C}$ , while that of methyl propanoate is only  $79^{\circ}\text{C}$  despite its higher relative formula mass. Explain the difference in the two boiling points.

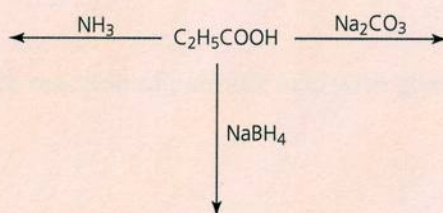
2 marks

d Propanoyl chloride may be used in place of propanoic acid for this preparation. State two advantages of using the acyl chloride.

2 marks

e Some reactions of propanoic acid are shown below. Draw the organic structure of the products of each reaction.

3 marks



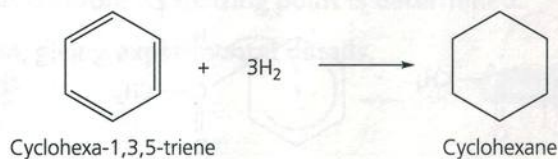


# Topic 10 Aromatic chemistry

## Bonding

Benzene is a *planar hexagonal* molecule of six carbon atoms. All carbon-carbon bond lengths are intermediate in length between that of a single C-C and a double C=C. Each carbon uses three of its outer electrons to form three sigma bonds to two other carbon atoms, and one hydrogen atom. This leaves each carbon atom with one electron in a *p* orbital. The *p* orbitals overlap sideways and the 6*p* electrons *delocalise* and give regions of electron density above and below the ring.

A theoretical cyclic compound with three double bonds is cyclohexa-1,3,5-triene, and it would be expected to have an enthalpy change of hydrogenation of  $-360 \text{ kJ mol}^{-1}$ , because three C=C bonds are being broken ( $3 \times -120 \text{ kJ mol}^{-1}$ ).

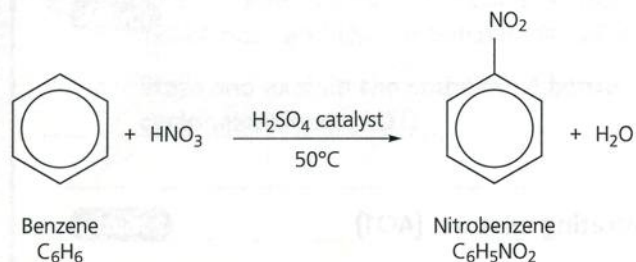


However, when benzene is hydrogenated the enthalpy change is only  $-208 \text{ kJ mol}^{-1}$ . This is  $152 \text{ kJ mol}^{-1}$  less than expected. This means that the actual structure of benzene is more stable than the theoretical cyclohexa-1,3,5-triene due to delocalisation of *p* electrons which are more spread out and so have fewer electron-electron repulsions.

## Electrophilic substitution

Benzene does not take part in addition reactions because this disrupts the delocalised ring. Instead it undergoes substitution reactions, where one or more of the hydrogen atoms is replaced by another atom or group.

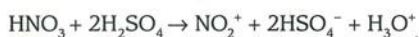
In nitration of benzene a nitro group ( $\text{NO}_2$ ) replaces one of the hydrogen atoms.



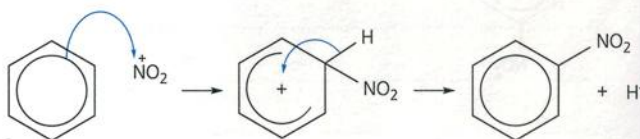
**Conditions:** concentrated sulfuric acid and concentrated nitric acid (nitrating mixture) at  $50^\circ\text{C}$ .

The mechanism is described as electrophilic substitution. The region of high electron density above and below the plane of the molecule results in the benzene being attacked by electrophiles, in this case  $\text{NO}_2^+$ .

The overall equation for the generation of the electrophile  $\text{NO}_2^+$  (nitronium ion) is:

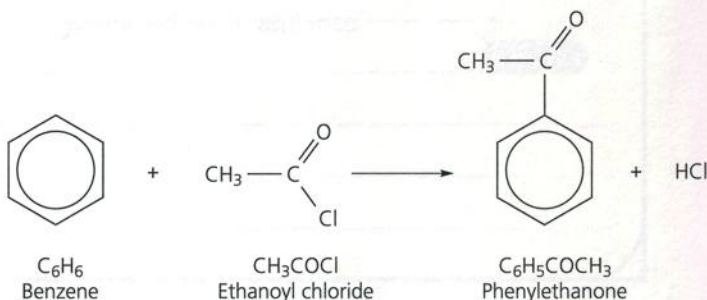


The mechanism for mononitration is shown below:



The concentrated sulfuric acid acts as a catalyst in the reaction as it is regenerated in the last step when an  $\text{H}^+$  ion is released in the mechanism and combines with  $\text{HSO}_4^-$  to reform sulfuric acid. Nitration is an important step in the manufacture of explosives such as TNT and in the formation of amines such as phenylamine to produce dyes.

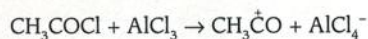
Benzene can be acylated using an acyl chloride, in the presence of a catalyst to form an aromatic ketone. This is an electrophilic substitution reaction in which an acyl group is attached to the ring. The equation for the acylation is:



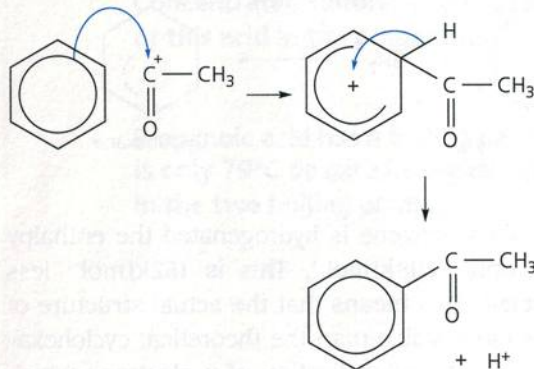


Conditions: catalyst of aluminium chloride, anhydrous conditions to prevent hydrolysis of the catalyst.

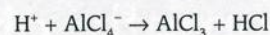
The required electrophile is the acylium ion:  $\text{CH}_3\text{-}\overset{+}{\text{C}}=\text{O}$ .  
The equation for the formation of the electrophile is:



The mechanism for acylation is:

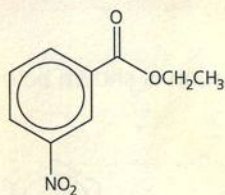


The catalyst is regenerated:



Friedel-Crafts acylation reactions are useful in synthesis, as the benzene forms a bond with a carbon, producing a side chain.

- 1** Ethyl 3-nitrobenzoate exists as a solid at room temperature and pressure. Its melting point is  $42^\circ\text{C}$ . It is prepared using a nitrating mixture.



- a** Write the equation for the formation of ethyl 3-nitrobenzoate from ethyl benzoate. (AO2)

1 mark

.....

.....

- b** Name the two chemicals which make up the nitrating mixture. (AO1)

2 marks

.....

.....

- c** Assuming a 70.0% yield, calculate the minimum mass of the organic reactant required to produce 5.85 g of ethyl 3-nitrobenzoate. (AO2)

3 marks

.....

.....

.....

.....





d Why can ethyl benzoate be nitrated to form a range of products? (AO2)

1 mark

e The crude ethyl 3-nitrobenzoate is recrystallised before its melting point is determined.

Explain why recrystallisation is carried out and, giving experimental details, describe the process of recrystallisation. (AO1)

4 marks

f How would the crystals be dried before the melting point is determined? (AO1)

1 mark

g How would you use the melting point to determine whether the crystals are pure ethyl 3-nitrobenzoate? (AO1)

2 marks

2 Cyclohexatriene is a hypothetical molecule. The enthalpy of hydrogenation of cyclohexene is  $-120 \text{ kJ mol}^{-1}$  and that of benzene is  $-208 \text{ kJ mol}^{-1}$ .

a State and explain the stability of benzene compared with the hypothetical cyclohexatriene. (AO1)

3 marks

b What is observed when bromine is bubbled into cyclohexatriene, and into benzene. (AO1)

2 marks



# Topic 11 Amines

A primary amine contains one alkyl or aryl group attached to the nitrogen atom, as only one hydrogen atom in ammonia has been replaced. A secondary amine contains two alkyl or aryl groups attached to the nitrogen atom, as two hydrogen atoms in ammonia have been replaced. A tertiary amine contains three alkyl or aryl groups attached to the nitrogen atom, as three hydrogen atoms in ammonia have been replaced.

Quaternary ammonium compounds have four alkyl groups attached to the nitrogen atom and are produced from tertiary amines when the nitrogen's lone pair of electrons forms a dative covalent bond to a fourth alkyl group. When naming amines, if you need to give the position of the carbon to which the  $\text{NH}_2$  group is attached, use the 'amino' form of naming.

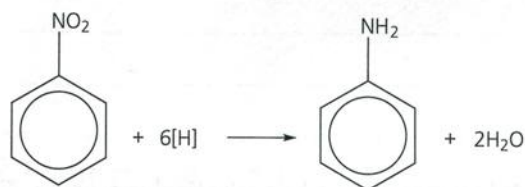
## Preparation

### Primary amines

	Equation	Condition
From halogenoalkanes	$\text{CH}_3\text{CH}_2\text{Cl} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Cl}$	Heat in a sealed flask with excess ammonia in ethanol. A sealed glass tube is used because the ammonia would escape as a gas if reflux was implemented.
From nitriles by reduction	$\text{CH}_3\text{CN} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$ ethanenitrile      ethylamine	Hydrogen in the presence of a nickel catalyst.
From nitriles by reduction	$\text{CH}_3\text{CH}_2\text{CN} + 4[\text{H}] \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ propanenitrile      propylamine	$[\text{H}]$ is lithium aluminium hydride in dry ether.

### Aromatic amines

Aromatic amines are prepared by reduction of nitrocompounds. For example, phenylamine is prepared by reduction of nitrobenzene using tin and concentrated hydrochloric acid as reducing agent. Aromatic amines prepared by the reduction of nitro compounds are used in the manufacture of dyes.




Nitrobenzene

Phenylamine

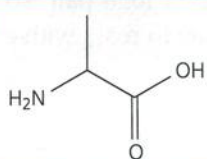
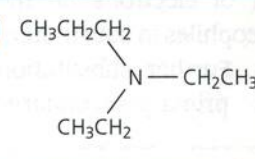
**Conditions:** heat under reflux with tin and excess concentrated hydrochloric acid, followed by adding concentrated sodium hydroxide.

### 1 Name the following structures (AO2)

10 marks

Structure	Structure
a $\text{CH}_3\text{CH}_2\text{NH}_2$	b $\text{CH}_3\text{CH}_2\text{CH}_2$   N—H   $\text{H}_3\text{C}$
c 	d $\text{CH}_3\text{CH}_2$   N—H   $\text{H}_3\text{C}$



Structure	Structure
e $\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_3$	f $\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_2 - \underset{\text{NH}_2}{\text{CH}} - \text{CH}_3$
g $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	h $(\text{CH}_3\text{CH})_2\text{NH}$
i 	j 

a

b

c

d

f

g

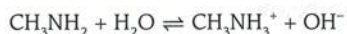
h

i

j

## Base properties of amines

Amines are weak bases (proton acceptors) because the lone pair of electrons on the nitrogen atom can accept a proton. They react with water, by accepting a hydrogen ion to produce an alkylammonium ion and hydroxide ions:



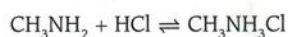
methylamine      methylammonium ion

The solution formed is weakly basic because the equilibrium lies to the left as methylamine is only partly

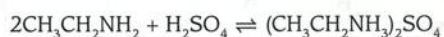
ionised and as a result little of it has reacted with the water, resulting in a solution with low  $[\text{OH}^-]$ .

Amines react with acid:

amine + acid  $\rightarrow$  alkyl ammonium salt



methylamine      methylammonium chloride



ethylamine      ethylammonium sulfate



Primary aliphatic amines are stronger bases than ammonia because of the electron-donating alkyl group attached to the nitrogen, meaning the electron density is increased, the lone pair is more available and so has an increased ability to accept a proton. Aliphatic amines generally increase in base strength

as the number of alkyl groups attached to the nitrogen atom increases. Primary aromatic amines are weaker bases than ammonia because nitrogen's lone pair of electrons is delocalised into the pi system, the electron density on the nitrogen is decreased and the lone pair is less available for accepting a proton.

## Nucleophilic properties

All amines contain a lone pair of electrons on the nitrogen atom, so they act as nucleophiles in substitution reactions with halogenoalkanes. Further substitution reactions may occur because the primary/secondary/

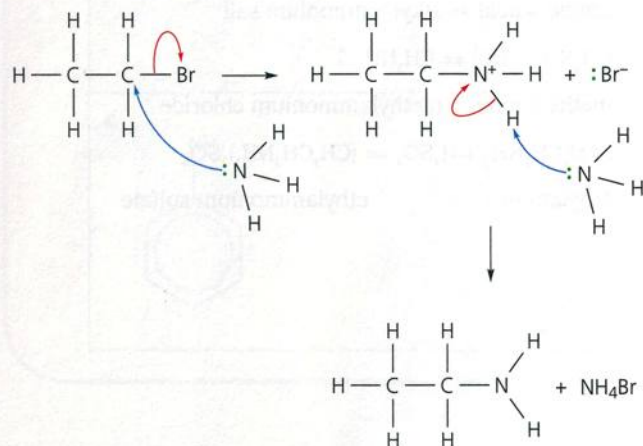
tertiary amine produced has a lone pair, so it can act as a nucleophile and continue to react with any unused halogenoalkane.

<b>Reaction to make a primary amine</b>	$\text{CH}_3\text{CH}_2\text{Cl} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Cl}$
<b>Reaction to make a secondary amine</b>	$\text{CH}_3\text{CH}_2\text{Br} + \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow (\text{CH}_3\text{CH}_2)_2\text{NH}_2\text{Br}$ diethylammonium bromide $(\text{CH}_3\text{CH}_2)_2\text{NH}_2\text{Br} + \text{NH}_3 \rightleftharpoons (\text{CH}_3\text{CH}_2)_2\text{NH} + \text{NH}_4\text{Br}$ diethylamine (secondary amine)
<b>Reaction to make a tertiary amine</b>	$\text{CH}_3\text{CH}_2\text{Br} + (\text{CH}_3\text{CH}_2)_2\text{NH} \rightarrow (\text{CH}_3\text{CH}_2)_3\text{NHBr}$ $(\text{CH}_3\text{CH}_2)_3\text{NHBr} + \text{NH}_3 \rightleftharpoons (\text{CH}_3\text{CH}_2)_3\text{N} + \text{NH}_4\text{Br}$ trimethylamine (tertiary amine)
<b>Reaction to make a quaternary ammonium salt</b>	$\text{CH}_3\text{CH}_2\text{Br} + (\text{CH}_3\text{CH}_2)_3\text{N} \rightarrow (\text{CH}_3\text{CH}_2)_4\text{NBr}$ quaternary ammonium salt

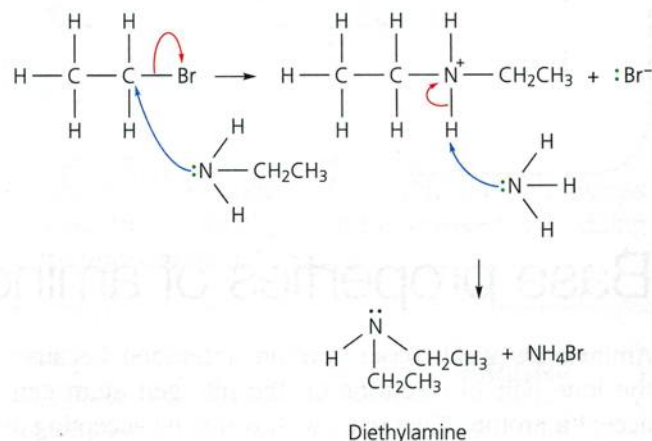
Excess ammonia favours the production of primary amines as it is less likely that another halogenoalkane molecule will react with an amine. When there is a large number of unreacted ammonia molecules available, excess halogenoalkane favours the production of the quaternary ammonium salts as it ensures that each ammonia reacts with four halogenoalkane molecules. Quaternary ammonium salts are used in the production of cationic surfactants.

### Mechanism

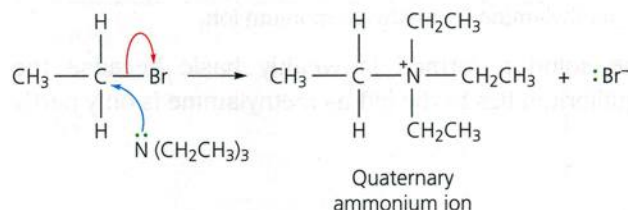
The reactions of a halogenoalkane with ammonia and amines forming primary, secondary, tertiary amines and quaternary ammonium salts are nucleophilic substitution reactions. The amines have lone pairs and are nucleophiles.



Further substitution is possible as the product, the primary amine, is also a nucleophile.



The mechanism for the formation of a quaternary ammonium ion is shown below:





**2 a** Write equations for the following reactions. (AO2)

**i** ethylamine and hydrochloric acid

1 mark

**ii** methylamine and sulfuric acid

1 mark

**iii** phenylamine and nitric acid

1 mark

**iv** ethylamine and water

1 mark

**v** ethylammonium chloride and sodium hydroxide

1 mark

**b** State and explain which of the following pairs is the stronger base. (AO2)

**i** ethylamine or ammonia

1 mark

**ii** phenylamine or ammonia

1 mark

**iii** ethylamine or butylamine

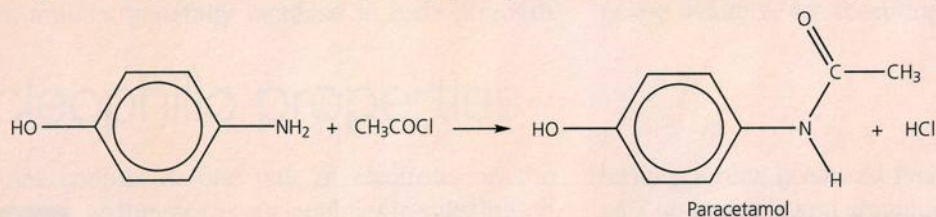
1 mark



## Exam-style questions



- 1 To produce paracetamol, 4-hydroxyphenylamine reacts with ethanoyl chloride:



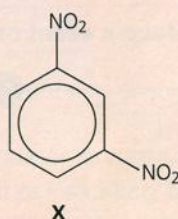
If the reaction has an 80% yield, 10.9 g of 4-hydroxyphenylamine reacts with excess ethanoyl chloride to produce what mass of paracetamol?

1 mark

- A 12.1 g of paracetamol  
B 13.6 g of paracetamol  
C 15.1 g of paracetamol  
D 18.9 g of paracetamol

- 2 a Name structure X.

1 mark



- b Name an isomer of X.

1 mark

- c X is prepared from nitrobenzene by reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid. The two acids react to form an inorganic species that reacts with nitrobenzene to form X.

- i Give the formula of this inorganic species formed from the two acids and write an equation to show its formation.

2 marks

- ii Name and outline a mechanism for the reaction of this inorganic species with nitrobenzene to form X.

4 marks



iii Give one reason why this reaction is useful in industry.

1 mark

d X can be reduced to a diamine.

Identify a suitable reagent or mixture of reagents for this reduction.

1 mark

3 In a Friedel–Crafts reaction ethanoyl chloride reacts with benzene.

a Write an equation for this reaction, and name the organic product.

2 marks

b Write an equation to show how the catalyst reacts with ethanoyl chloride to produce a reactive intermediate.

1 mark

c Outline the mechanism for the reaction of benzene with the reactive intermediate.

3 marks

4 Amines have characteristic fishy smells. They act as nucleophiles.

a State and explain why amines can act as nucleophiles.

2 marks

b Write an equation for the reaction of 1-bromopropane with excess ammonia.

1 mark

c Name the type of compound produced when a large excess of 1-bromopropane reacts with methylamine.

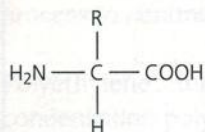
1 mark



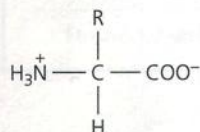
# Topic 13 Amino acids, proteins and DNA

## Amino acids

An amino acid contains a COOH group and an NH<sub>2</sub> group. There are 20 naturally occurring amino acids, which can be divided into non-polar, polar, acidic and basic. The basic structure of an amino acid is shown below, where R represents the side chain. Glycine is the simplest amino acid where R = H and glycine does not show optical activity. All other amino acids do.



Amino acids exist as dipolar ions (or zwitterions). The general structure of the zwitterion is shown below. In acidic solution the amino acid will be a positively charged ion; in alkaline solution the amino acid will be a negatively charged ion.



Solid amino acids contain ionic bonds and so have higher than expected melting points for relatively small organic compounds.

## Proteins

Amino acids react together to form peptide groups (-CO-NH-). The primary structure of a protein is a sequence of amino acids connected by peptide groups. Proteins are polyamide condensation polymers. The secondary structure of a protein is made up of alpha helices and beta pleated sheets where the chain of amino acids twists into a helix or a series of loops all held together by hydrogen bonds between the C=O and N-H bonds in different parts of the chain. The tertiary

structure of a protein is the final folding of the protein molecule, which is held together by ionic interactions, disulfide bridges, hydrophobic/hydrophilic interactions and hydrogen bonds.

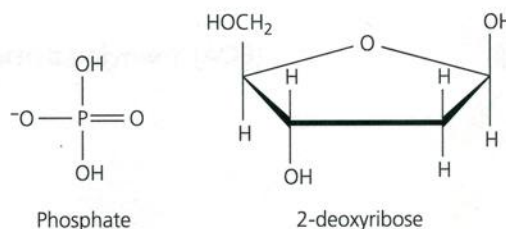
## Enzymes

Enzymes are proteins which act as biological catalysts. Enzymes react with substrate molecules, turning them into products. The substrate molecules sit in the active site in the molecule, and groups in the active site catalyse the reaction. Enzymes are stereospecific, so will only catalyse the reaction for one stereoisomer. Enzymes may be inhibited by blocking the active site with a different molecule. Enzymes are temperature and pH dependent. They are denatured at high temperatures, rendering the enzyme inactive.

Proteins may be hydrolysed to form a mixture of amino acids, which may be separated by chromatography.

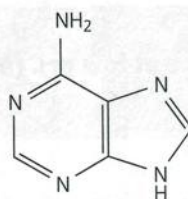
## DNA

DNA is a polymer made up of a chain of 2-deoxyribose sugar molecules connected by phosphate groups. Also bonded to each sugar is a base. Two strands of the polymer join together as they form hydrogen bonds between complementary bases in the strands. DNA is built up from nucleotides which are molecules consisting of the 2-deoxyribose sugar, the phosphate group and the base.

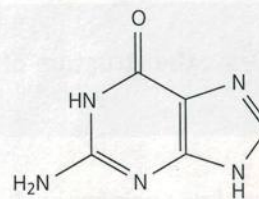




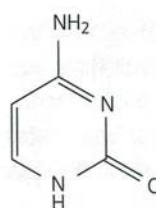
The four bases in DNA are adenine (A), cytosine (C), guanine (G) and thymine (T). The letters A, C, G and T are often used to represent them in shorthand. Guanine pairs with cytosine and adenine with thymine. Three hydrogen bonds form between G and C base pairs, whereas two hydrogen bonds form between A and T base pairs.



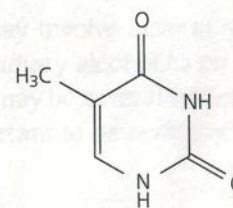
Adenine



Guanine

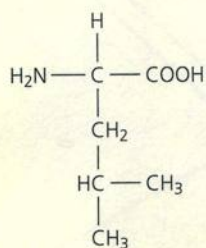


Cytosine

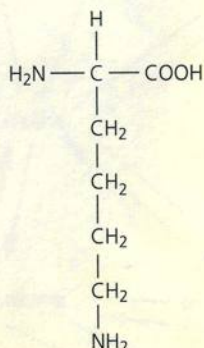


Thymine

**1** Leucine and lysine have the following structures:



Leucine



Lysine

**a** Give the IUPAC name for leucine. (AO2)

1 mark

**b** Give the IUPAC name for lysine. (AO2)

1 mark

**c** Draw the structure of two dipeptides formed from leucine and lysine. Circle the peptide group in each peptide. (AO3)

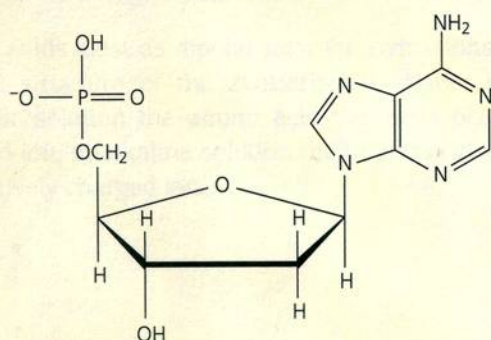
4 marks



d Draw the structure of lysine at low pH. (AO2)

1 mark

2 The structure below shows a nucleotide.



a i On the diagram label the position 2 of 2-deoxyribose. (AO1)

1 mark

ii Name the base in this nucleotide. (AO1)

1 mark

iii Name the base to which adenine bonds in the double-stranded DNA molecule. (AO1)

1 mark

iv State the type of polymerisation which occurs between nucleotides. (AO1)

1 mark

b Write the formula of the complex cisplatin and explain how cisplatin acts as an anticancer drug in terms of its interaction with DNA. (AO2)

4 marks

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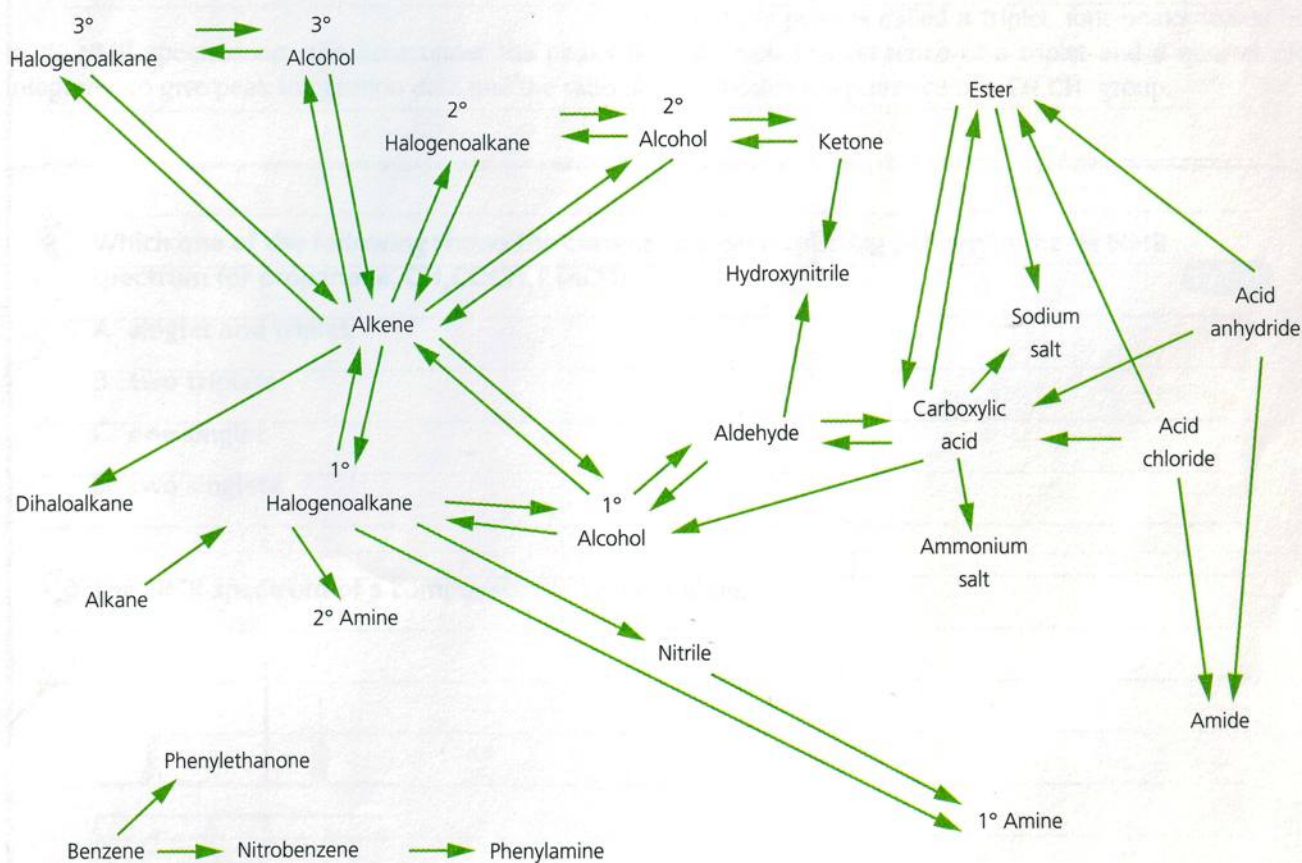
# Topic 14 Organic synthesis

Organic synthesis allows different organic compounds to be converted into others using chemical reactions. The diagram below shows the different types of organic chemicals and the arrows show the chemical reactions which may be used to convert one into another.

It is important to know the type of reaction occurring and to be able to write equations for these reactions.

Also it is vital to recall the conditions and reagents that are used for the reactions.

A synthetic pathway may involve several steps from a halogenoalkane to a primary alcohol to an aldehyde to a hydroxynitrile. There may be several routes which may be taken and it is important to be aware of the number of steps in each route.





Route A is a two-stage process that starts with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ .

Route B is a one-stage process that starts with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ .

Identify the intermediate compound in route A.

Give the reagents and conditions for both stages in route A and the single stage in route B.

7 marks