

Functional groups and homologous series

NAMING ORGANIC COMPOUNDS

Organic chemistry is concerned with the compounds of carbon. Since there are more compounds of carbon known than all the other elements put together, it is helpful to have a systematic way of naming them.

1. Identify the longest carbon chain.

- 1 carbon = **meth-**
- 2 carbons = **eth-**
- 3 carbons = **prop-**
- 4 carbons = **but-**
- 5 carbons = **pent-**
- 6 carbons = **hex-**
- 7 carbons = **hept-**
- 8 carbons = **oct-**

2. Identify the type of bonding in the chain or ring

- All single bonds in the carbon chain = **-an-**
- One double bond in the carbon chain = **-en-**
- One triple bond in the carbon chain = **-yn-**

3. Identify the functional group joined to the chain or ring.

This may come at the beginning or at the end of the name, e.g.

alkane: only hydrogen (-H) joined to chain = **-e**

alcohol: -OH = **-ol**

amine: -NH₂ = **amino-**

halogenoalkane: -X: **chloro-, bromo, or iodo-**

aldehyde: $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-H} \end{array}$ (on the end of the chain) = **-al**

ketone: $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-} \end{array}$ (not on the end of the chain) = **-one**

carboxylic acid: $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-OH} \end{array}$ = **-oic acid**

ester: $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-OR} \end{array}$ = **-oate**

4. Numbers are used to give the positions of groups or bonds along the chain.

HOMOLOGOUS SERIES

The alkanes form a series of compounds all with the general formula C_nH_{2n+2}, e.g.

methane CH₄

ethane C₂H₆

propane C₃H₈

butane C₄H₁₀

If one of the hydrogen atoms is removed what is left is known as an alkyl radical R- (e.g. methyl CH₃-; ethyl C₂H₅-).

When other atoms or groups are attached to an alkyl radical they can form a different series of compounds.

These atoms or groups attached are known as functional groups and the series formed are all homologous series.

Homologous series have the same general formula with the neighbouring members of the series differing by -CH₂; for example the general formula of alcohols is C_nH_{2n+1}OH. The chemical properties of the individual members of an homologous series are similar and they show a gradual change in physical properties.

SOME COMMON FUNCTIONAL GROUPS

Formula	Name	Examples
R-H	alkane	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \\ \text{methane} \end{array}$ $\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \\ \text{butane} \end{array}$ $\begin{array}{c} & & & \text{H} \\ & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \\ \text{2-methylpropane} \end{array}$
R-OH	alcohol	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{O}-\text{H} \\ & \\ \text{H} & \text{H} \\ \text{ethanol} \end{array}$ $\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{O}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \\ \text{propan-1-ol} \end{array}$ $\begin{array}{c} & & & \text{H} & \text{O}-\text{H} \\ & & & & \\ \text{H} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \\ \text{propan-2-ol} \end{array}$
R-NH ₂	amine	$\begin{array}{c} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{N}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \\ \text{ethylamine (aminoethane)} \end{array}$ $\begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & \text{H} & \text{H} & \text{H} \\ \text{2-aminobutane} \end{array}$
R-X (X = F, Cl, Br, or I)	halogenoalkane	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{Br} \\ & \\ \text{H} & \text{H} \\ \text{bromoethane} \end{array}$ $\begin{array}{c} \text{Cl} & \text{Cl} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \\ \text{1,2-dichloroethane} \end{array}$ $\begin{array}{c} \text{Cl} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{Cl} & \text{H} \\ \text{1,1-dichloroethane} \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array}$	aldehyde	$\begin{array}{c} \text{H} & \text{O} \\ & \parallel \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \\ \text{ethanal} \end{array}$ $\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{C}-\text{H} \\ & & \parallel \\ \text{H} & \text{H} & \text{O} \\ \text{propanal} \end{array}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$ (R' may be the same as or different to R)	ketone	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{CH}_3$ propanone $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_3$ pentan-2-one $\text{H}_3\text{C}-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_3$ pentan-3-one
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$	carboxylic acid	$\begin{array}{c} \text{H} & \text{O} \\ & \parallel \\ \text{H}-\text{C} & -\text{C}-\text{O}-\text{H} \\ & \\ \text{H} & \text{H} \\ \text{methanoic acid} \end{array}$ $\text{C}_2\text{H}_5-\text{C}(=\text{O})-\text{O}-\text{H}$ propanoic acid
$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR}' \end{array} \right]$	ester	$\begin{array}{c} \text{H} & \text{O} & \text{H} & \text{H} \\ & \parallel & & \\ \text{H}-\text{C} & -\text{C}-\text{O}-\text{C} & -\text{C}-\text{H} \\ & & & \\ \text{H} & & \text{H} & \text{H} \\ \text{ethyl ethanoate} \end{array}$ $\text{H}-\text{C}(=\text{O})-\text{O}-\text{C}_2\text{H}_5$ propyl methanoate

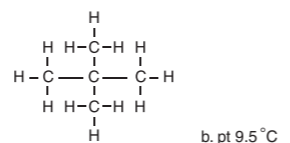
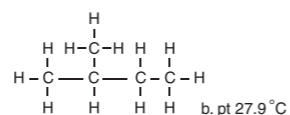
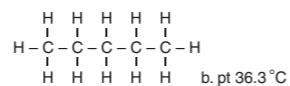
Properties of different functional groups

BOILING POINTS

As the carbon chain gets longer the mass of the molecules increases and the van der Waals' forces of attraction increase. A plot of boiling point against number of carbon atoms shows a sharp increase at first, as the percentage increase in mass is high, but as successive $-\text{CH}_2-$ groups are added the rate of increase in boiling point decreases.

When branching occurs the molecules become more spherical in shape, which reduces the contact surface area between them and lowers the boiling point.

Other homologous series show similar trends but the actual temperatures at which the compounds boil will depend on the types of attractive forces between the molecules. The volatility of the compounds also follows the same pattern. The lower members of the alkanes are all gases as the attractive forces are weak and the next few members are volatile liquids. Methanol, the first member of the alcohols is a liquid at room temperature, due to the presence of hydrogen bonding. Methanol is classed as volatile as its boiling point is 64.5°C but when there are four or more carbon atoms in the chain the boiling points exceed 100°C and the higher alcohols have low volatility.



Compound	Formula	M_r	Functional group	Strongest type of attraction	B. pt / $^\circ\text{C}$
butane	C_4H_{10}	58	alkane	van der Waals'	-0.5
butene	C_4H_8	56	alkene	van der Waals'	-6.2
butyne	C_4H_6	54	alkyne	van der Waals'	8.1
methyl methanoate	HCOOCH_3	60	ester	dipole:dipole	31.5
propanal	$\text{CH}_3\text{CH}_2\text{CHO}$	58	aldehyde	dipole:dipole	48.8
propanone	CH_3COCH_3	58	ketone	dipole:dipole	56.2
aminopropane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	59	amine	hydrogen bonding	48.6
propan-1-ol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	60	alcohol	hydrogen bonding	97.2
ethanoic acid	CH_3COOH	60	carboxylic acid	hydrogen bonding	118

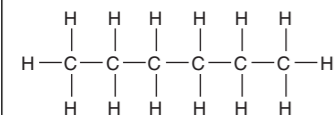
SOLUBILITY IN WATER

Whether or not an organic compound will be soluble in water depends on the polarity of the functional group and on the chain length. The lower members of alcohols, amines, aldehydes, ketones, and carboxylic acids are all water soluble. However, as the length of the non-polar hydrocarbon chain increases the solubility in water decreases. For example, ethanol and water mix in all proportions, but hexan-1-ol is only slightly soluble in water. Compounds with non-polar functional groups, such as alkanes, and alkenes, do not dissolve in water but are soluble in other non-polar solvents. Propan-1-ol is a good solvent because it contains both polar and non-polar groups and can to some extent dissolve both polar and non-polar substances.

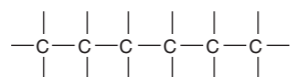
STRUCTURAL FORMULAS

The difference between the empirical, molecular and structural formulas of a compound has been covered in Topic 1 - quantitative chemistry. Because the physical and chemical properties of organic compounds are determined by the functional group and the arrangement of carbon atoms within the molecule, the structural formulas for organic compounds are often used.

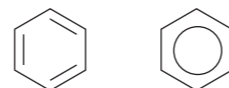
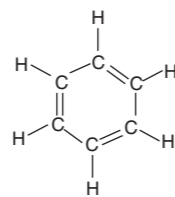
The structural formula unambiguously shows how the atoms are bonded together. All the hydrogen atoms must be shown when drawing organic structures. The skeletal formula showing just the carbon atoms without the hydrogen atoms is not acceptable except for benzene (see below). However, unless specifically asked, Lewis structures showing all the valence electrons are not necessary. The bonding must be clearly indicated. Structures may be shown using lines as bonds or in their shortened form e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ for pentane but the molecular formula C_5H_{12} will not suffice.



structural formula of hexane
also acceptable
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
and $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$



skeletal formula of hexane
not acceptable as structural formula



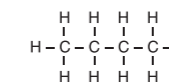
three different ways of showing the structural formula of benzene, all are acceptable

Structural isomers

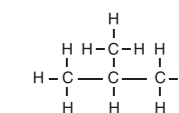
STRUCTURES OF HYDROCARBONS

Isomers of alkanes

Each carbon atom contains four single bonds. There is only one possible structure for each of methane, ethane, and propane however two structures of butane are possible.



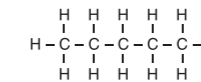
butane



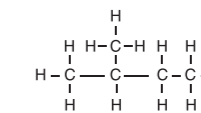
2-methylpropane

These are examples of structural isomers.

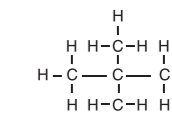
Structural isomers have the same molecular formula but a different structural formula. They normally have similar chemical properties but their physical properties may be slightly different. There are three structural isomers of pentane.



pentane
(b. pt 36.3°C)



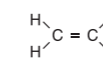
2-methylbutane
(b. pt 27.9°C)



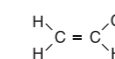
2,2-dimethylpropane
(b. pt 9.5°C)

Structures of alkenes

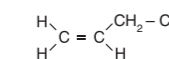
Ethene and propene only have one possible structure each but butene has three structural isomers.



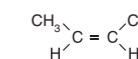
ethene



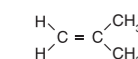
propene



but-1-ene



but-2-ene

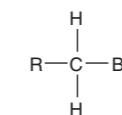
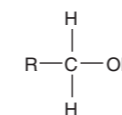


2-methylpropene

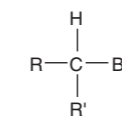
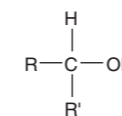
CLASSIFICATION OF ALCOHOLS AND HALOGENOALKANES

Alcohols and halogenoalkanes may be classified according to how many R- groups and how many hydrogen atoms are bonded to the carbon atom containing the functional group.

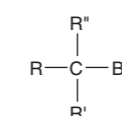
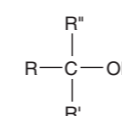
primary (on R-group bonded to C atom)



secondary (two R-group bonded to C atom)
R may be the same as R' or different



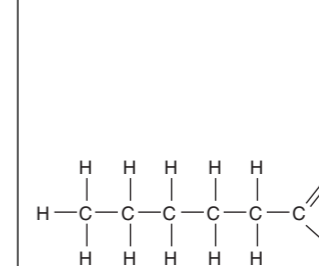
Tertiary (three R-group bonded to C atom)



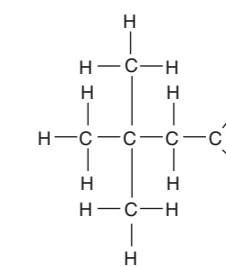
NAMING STRUCTURAL ISOMERS

The naming system explained on page 61 is known as the IUPAC (International Union of Pure and Applied Chemistry) system. The IUPAC names to distinguish between structural isomers of alcohols, aldehydes, ketones, carboxylic acids and halogenoalkanes containing up to six carbon atoms are required.

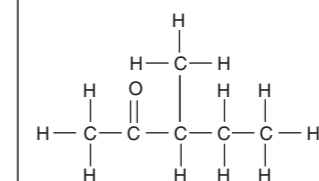
For example, four different structural isomers with the molecular formula $\text{C}_6\text{H}_{12}\text{O}$ are shown.



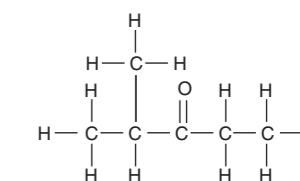
or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
hexanal



$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CHO}$
3,3-dimethylbutanal



or $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
3-methylpentan-2-one



or $\text{CH}_3\text{CH}(\text{CH}_3)\text{COCH}_2\text{CH}_3$
2-methylpentan-3-one

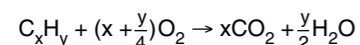
Alkanes

LOW REACTIVITY OF ALKANES

Because of the relatively strong C–C and C–H bonds and because they have low polarity, alkanes tend to be quite unreactive. They only readily undergo combustion reactions with oxygen and substitution reactions with halogens in ultraviolet light.

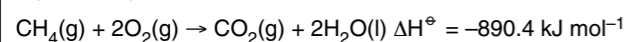
COMBUSTION

Alkanes are hydrocarbons - compounds that contain carbon and hydrogen only. All hydrocarbons burn in a plentiful supply of oxygen to give carbon dioxide and water. The general equation for the combustion of any hydrocarbon is:

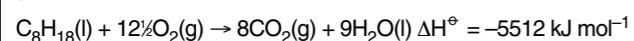


Although the C–C and C–H bonds are strong the C=O and O–H bonds in the products are even stronger so the reaction is very exothermic and much use is made of the alkanes as fuels.

e.g natural gas (methane)



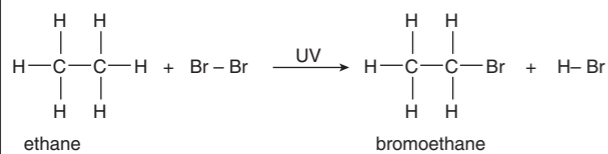
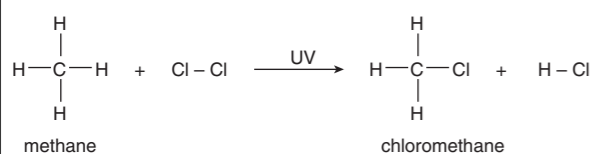
gasoline (petrol)



If there is an insufficient supply of oxygen then incomplete combustion occurs and carbon monoxide and carbon are also produced as products.

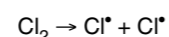
SUBSTITUTION REACTIONS

Alkanes can react with chlorine (or other halogens) in the presence of ultraviolet light to form hydrogen chloride and a substituted alkane, e.g. methane can react with chlorine to form chloromethane and ethane can react with bromine to form bromoethane.



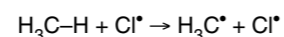
MECHANISM OF CHLORINATION OF METHANE

The mechanism of an organic reaction describes the individual steps. When chemical bonds break they may break **heterolytically** or **homolytically**. In heterolytic fission both of the shared electrons go to one of the atoms resulting in a negative and a positive ion. In homolytic fission each of the two atoms forming the bond retains one of the shared electrons resulting in the formation of two **free radicals**. The bond between two halogen atoms is weaker than the C–H or C–C bond in methane and can break homolytically in the presence of ultraviolet light.

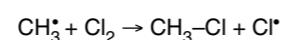


This stage of the mechanism is called **initiation**.

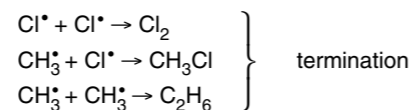
Free radicals contain an unpaired electron and are highly reactive. When the chlorine free radicals come into contact with a methane molecule they combine with a hydrogen atom to produce hydrogen chloride and a methyl radical.



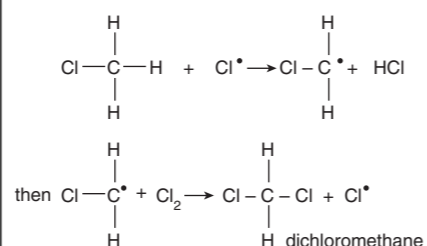
Since a new radical is produced this stage of the mechanism is called **propagation**. The methyl free radical is also extremely reactive and reacts with a chlorine molecule to form the product and regenerate another chlorine radical. This is a further propagation step and enables a chain reaction to occur as the process can repeat itself.



In theory a single chlorine radical may cause up to 10 000 molecules of chloromethane to be formed. **Termination** occurs when two radicals react together.



Further substitution can occur when chlorine radicals react with the substituted products. For example:



The substitution can continue even further to produce trichloromethane and then tetrachloromethane.

The overall mechanism is called **free radical substitution**. [Note that in this mechanism hydrogen radicals H[•] are not formed.]

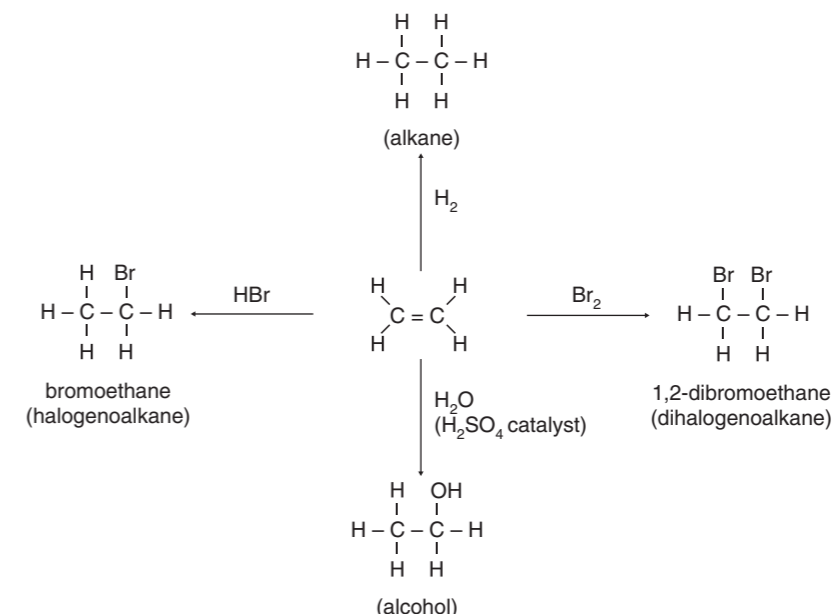
Alkenes

ADDITION REACTIONS

The bond enthalpy of the C=C double bond in alkenes has a value of 612 kJ mol⁻¹. This is less than twice the average value of 348 kJ mol⁻¹ for the C–C single bond and accounts for the relative reactivity of alkenes compared to alkanes. The most important reactions of alkenes are addition reactions. Reactive molecules are able to add across the double bond. The double bond is said to be **unsaturated** and the product, in which each carbon atom is bonded by four single bonds, is said to be **saturated**.



Addition reactions include the addition of hydrogen, bromine, hydrogen halides, and water.



USES OF ADDITION REACTIONS

1. Bromination

Pure bromine is a red liquid but it has a distinctive yellow/orange colour in solution. When a solution of bromine is added to an alkene the product is colourless. This decolorization of bromine solution provides a useful test to indicate the presence of an alkene group.

2. Hydration

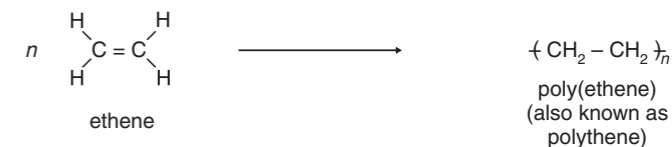
Ethene is an important product formed during the cracking of oil. Although ethanol can be made from the fermentation of starch and sugars, much industrial ethanol is formed from the addition of steam to ethene.

3. Hydrogenation

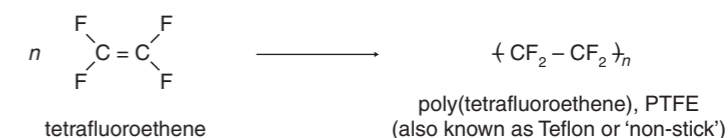
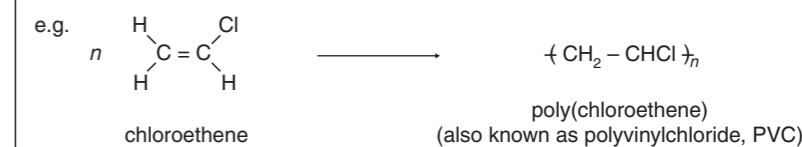
The addition of hydrogen to unsaturated vegetable oils is used industrially to make margarine. Hydrogenation reduces the number of double bonds in the polyunsaturated vegetable oils present in the margarine, which causes it to become a solid at room temperature.

ADDITION POLYMERIZATION

Under certain conditions ethene can also undergo addition reactions with itself to form a long chain polymer containing many thousands (typically 40 000 to 800 000) of carbon atoms.



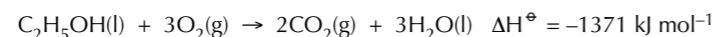
These addition reactions can be extended to other substituted alkenes to give a wide variety of different addition polymers.



Alcohols

COMBUSTION

Ethanol is used both as a solvent and as a fuel. It combusts completely in a plentiful supply of oxygen to give carbon dioxide and water.



Ethanol is already partially oxidized so it releases less energy than burning an alkane of comparable mass. However, it can be obtained by the fermentation of biomass so in some countries it is mixed with petrol to produce 'gasohol' which decreases the dependence on crude oil.

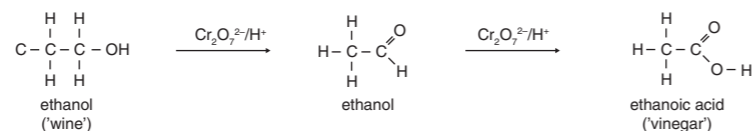
The general equation for an alcohol combusting completely in oxygen is:



OXIDATION OF ETHANOL

Ethanol can be readily oxidized by warming with an acidified solution of potassium dichromate(VI). During the process the orange dichromate(VI) ion $\text{Cr}_2\text{O}_7^{2-}$ is reduced from an oxidation state of +6 to the green Cr^{3+} ion. Use is made of this in simple breathalyser tests, where a

motorist who is suspected of having exceeded the alcohol limit blows into a bag containing crystals of potassium dichromate(VI).



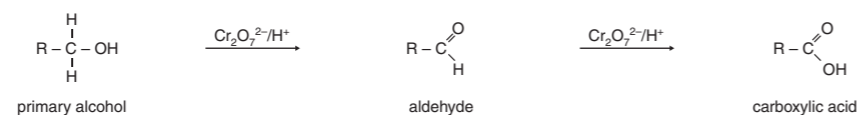
Ethanol is initially oxidized to ethanal. The ethanal is then oxidized further to ethanoic acid.

Unlike ethanol (b. pt 78.5 °C) and ethanoic acid (b. pt 118 °C) ethanal (b. pt 20.8 °C) does not have hydrogen bonding between its molecules, and so has a lower boiling point. To stop the reaction at the aldehyde stage the ethanal can be distilled from the reaction mixture as soon as it is formed. If the complete oxidation to ethanoic acid is required, then the mixture can be heated under reflux so that none of the ethanal can escape.

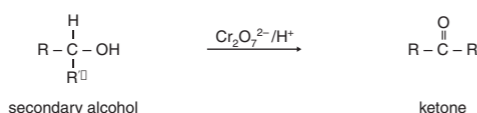
OXIDATION OF ALCOHOLS

Ethanol is a primary alcohol, that is the carbon atom bonded to the -OH group is bonded to two hydrogen atoms and one alkyl group. The oxidation reactions of alcohols can be used to distinguish between primary, secondary, and tertiary alcohols.

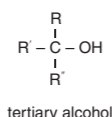
All **primary alcohols** are oxidized by acidified potassium dichromate(VI), first to aldehydes then to carboxylic acids.



Secondary alcohols are oxidized to ketones, which cannot undergo further oxidation.



Tertiary alcohols cannot be oxidized by acidified dichromate(VI) ions as they have no hydrogen atoms attached directly to the carbon atom containing the -OH group. It is not true to say that tertiary alcohols can never be oxidized, as they burn readily, but when this happens the carbon chain is destroyed.



Substitution reactions and reaction pathways

SUBSTITUTION REACTIONS OF HALOGENOALKANES

Because of the greater electronegativity of the halogen atom compared with the carbon atom halogenoalkanes have a polar bond. Reagents that have a non-bonding pair of electrons are attracted to the carbon atom in halogenoalkanes and a substitution reaction occurs. Such reagents are called **nucleophiles**

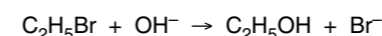


A double-headed curly arrow represents the movement of a pair of electrons. It shows where they come from and where they move to.

MECHANISM OF NUCLEOPHILIC SUBSTITUTION

Primary halogenoalkanes (one alkyl group attached to the carbon atom bonded to the halogen)

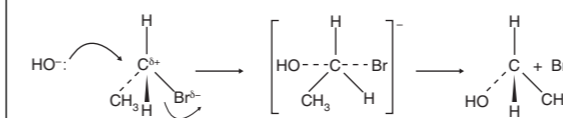
e.g. the reaction between bromoethane and warm dilute sodium hydroxide solution.



The experimentally determined rate expression is:

$$\text{rate} = k[\text{C}_2\text{H}_5\text{Br}][\text{OH}^-]$$

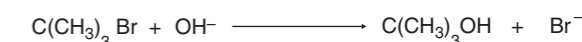
The proposed mechanism involves the formation of a transition state which involves both of the reactants.



Because the molecularity of this single-step mechanism is two it is known as an $\text{S}_{\text{N}}2$ mechanism (bimolecular nucleophilic substitution).

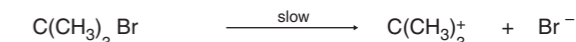
Tertiary halogenoalkanes (three alkyl groups attached to the carbon atom bonded to the halogen)

e.g. the reaction between 2-bromo-2-methylpropane and warm dilute sodium hydroxide solution.



The experimentally determined rate expression for this reaction is: $\text{rate} = k[\text{C}(\text{CH}_3)_3\text{Br}]$

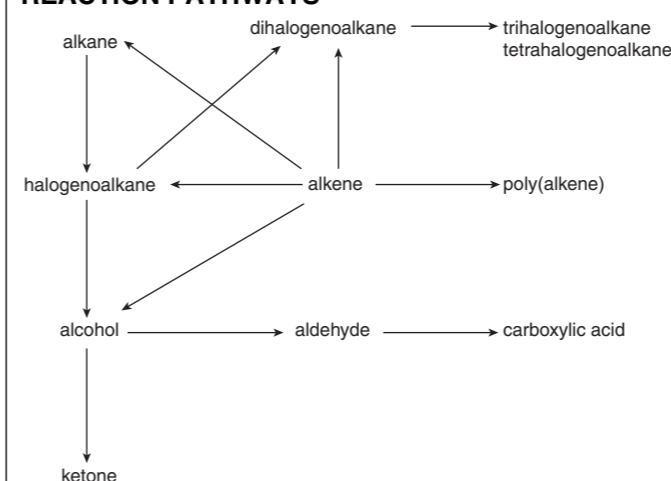
A two-step mechanism is proposed that is consistent with this rate expression.



In this reaction it is the first step that is the rate determining step. The molecularity of this step is one and the mechanism is known as $\text{S}_{\text{N}}1$ (unimolecular nucleophilic substitution).

The mechanism for the hydrolysis of secondary halogenoalkanes (e.g. 2-bromopropane $\text{CH}_3\text{CHBrCH}_3$) is more complicated as they can proceed by either $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ pathways or a combination of both.

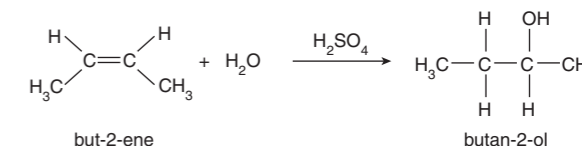
REACTION PATHWAYS



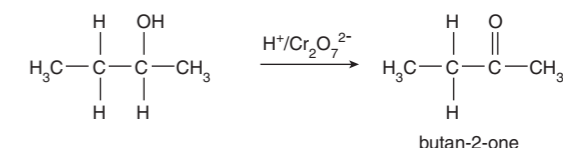
Using the scheme on the left which summarizes the organic reactions in the text, it is possible to devise reaction pathways. These should involve no more than two steps and should include the reagents, conditions and relevant equations.

e.g. to convert but-2-ene to butanone

Step 1. Heat but-2-ene in the presence of H_2SO_4 as a catalyst to form butan-2-ol



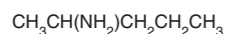
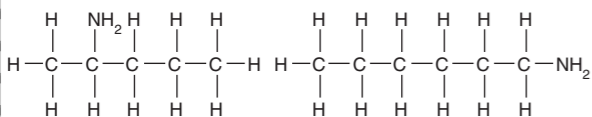
Step 2. Oxidize butan-2-ol to but-2-one by warming with acidified potassium dichromate(VI) solution



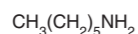
HL Identifying and naming more functional groups

AMINES (R-NH₂)

IUPAC accepts several different ways of naming amines. The most straightforward system is to prefix the longest chain alkane by the word amino- with the location of the NH₂-group being indicated. For example, 2-aminopentane and 1-aminohexane. It is also correct to call them by the longest alkane with the suffix -amine e.g. pentan-2-amine. If the number of carbon atoms is small (one, two or three) then the old names of methylamine, ethylamine and propylamine tend to be used rather than aminomethane, aminoethane and aminopropane. IUPAC accepts 1-butylamine, 1-butanamine and 1-aminobutane for CH₃CH₂CH₂CH₂NH₂.

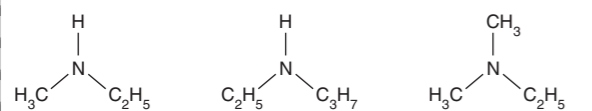


2-aminopentane
(or pentan-2-amine)



1-aminohexane
(or hexan-1-amine)

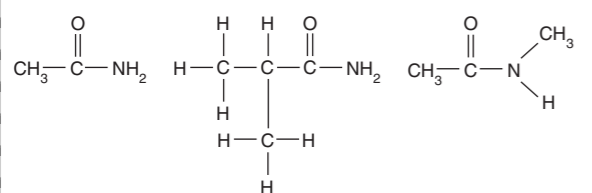
For secondary amines the main name of the amine is taken from the longest carbon chain attached to the nitrogen atom. The other chain is prefixed as an alkyl group with the location prefix given as an italic *N*. Examples include *N*-methylethanamine and *N*-ethylpropanamine. Tertiary amines contain two prefixes with an italic *N*, for example CH₃CH₂N(CH₃)₂ is *N,N*-dimethylethanamine.



N-methylethanamine *N*-ethylpropanamine *N,N*-dimethylethanamine

AMIDES (R-CO-NH₂)

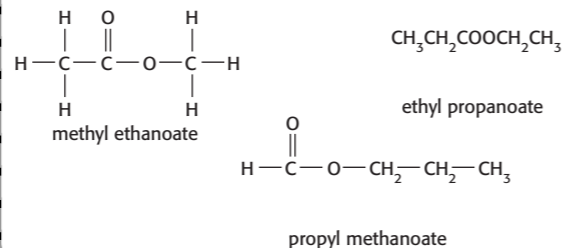
Amides are named after the longest carbon chain (which includes the carbon atom in the functional group) followed by -amide. For example, ethanamide and 2-methylpropanamide. Secondary amides are named rather like amines in that the other alkyl group attached to the nitrogen atom is prefixed by an *N*, e.g., *N*-methylethanamide.



ethanamide 2-methylpropanamide *N*-methylethanamide

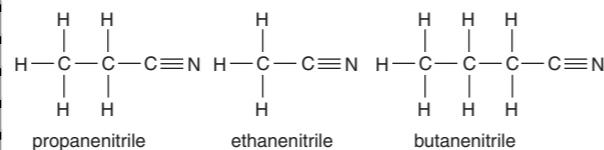
ESTERS (R-COO-R')

Esters take their IUPAC name from the acid and alcohol from which they are derived. The first part of the ester is named after the R- group from the alcohol. There is then a space followed by the name for the carboxylic acid anion. For example, methyl ethanoate, ethyl propanoate and propyl methanoate.



NITRILES (R-CN)

Nitriles used to be called cyanides so that C₂H₅CN was known as ethyl cyanide. IUPAC bases the name on the longest carbon chain (which includes the carbon atom of the nitrile group) with the word -nitrile is added to the alkane. For example, the IUPAC name for C₂H₅CN is propanenitrile. Ethanenitrile has the formula CH₃CN, and butanenitrile the formula C₃H₇CN.



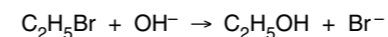
propanenitrile ethanenitrile butanenitrile

HL Nucleophilic substitution

NUCLEOPHILIC SUBSTITUTION

The reaction between halogenoalkanes and a warm dilute aqueous solution of sodium hydroxide is a nucleophilic substitution reaction. Other nucleophiles are CN⁻, NH₃ and H₂O. The nucleophiles are attracted to the δ⁺ carbon atom and substitute the halogen atom in halogenoalkanes.

Primary halogenoalkanes react by an S_N2 mechanism:



and tertiary halogenoalkanes react by an S_N1 mechanism.

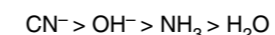


There are several factors which affect the rate of the substitution reactions.

FACTORS AFFECTING THE RATE OF NUCLEOPHILIC SUBSTITUTION

THE NATURE OF THE NUCLEOPHILE

The effectiveness of a nucleophile depends on its electron density. Anions tend to be more reactive than the corresponding neutral species. For example, the rate of substitution with the hydroxide ion is faster than with water. Among species with the same charge a less electronegative atom carrying a non bonded pair of electrons is a better nucleophile than a more electronegative one. Thus ammonia is a better nucleophile than water. This is because the less electronegative atom can more easily donate its pair of electrons as they are held less strongly.



order of reactivity of common nucleophiles

THE NATURE OF THE HALOGEN

For both S_N1 and S_N2 reactions the iodoalkanes react faster than bromoalkanes, which in turn react faster than chloroalkanes. This is due to the relative bond energies, as the C-I bond is much weaker than the C-Cl bond and therefore breaks more readily.

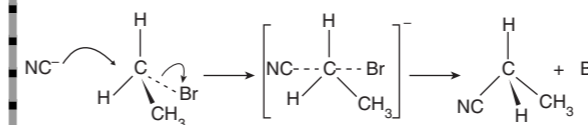
Bond enthalpy / kJ mol⁻¹

C-I	238
C-Br	276
C-Cl	338

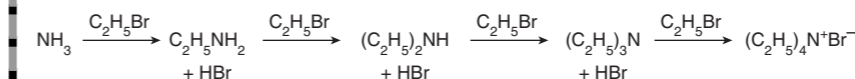
THE NATURE OF THE HALOGENOALKANE

Tertiary halogenoalkanes react faster than secondary halogenoalkanes, which in turn react faster than primary halogenoalkanes. The S_N1 route, which involves the formation of an intermediate carbocation, is faster than the S_N2 route, which involves a transition state with a relatively high activation energy.

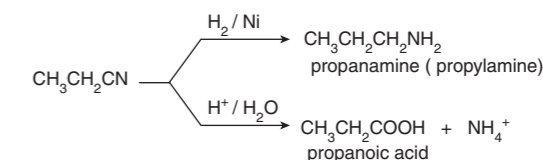
In addition to forming alcohols when water or hydroxide ions are used as the nucleophile, halogenoalkanes can react with ammonia to form amines and with cyanide ions to form nitriles. With primary halogenoalkanes the mechanism is S_N2 in both cases, e.g. with bromoethane and cyanide ions propanenitrile is produced.



When bromoethane reacts with ammonia, ethylamine is produced. However ethylamine also contains a nitrogen atom with a non-bonding pair of electrons so this too can act as a nucleophile and secondary and tertiary amines can be formed. Even the tertiary amine is still a nucleophile and can react further to form the quaternary salt.



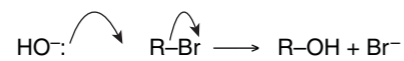
The nucleophilic substitution reactions of halogenoalkanes makes them particularly useful in organic synthesis. The reaction with potassium cyanide provides a useful means of increasing the length of the carbon chain by one carbon atom. The nitrile can then be converted either into amines by reduction using hydrogen with a nickel catalyst or into carboxylic acids by acid hydrolysis, e.g.



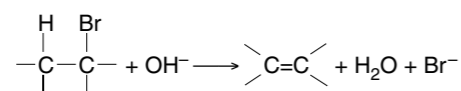
Elimination and condensation reactions

ELIMINATION REACTIONS OF HALOGENOALKANES

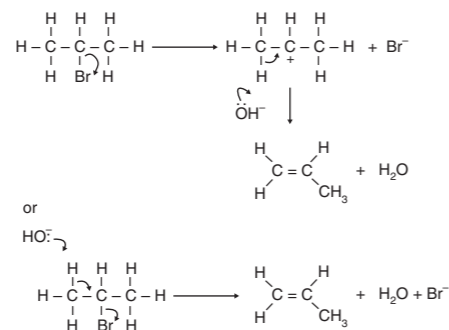
The reactions of halogenoalkanes with hydroxide ions provide an example of how altering the reaction conditions can cause the same reactants to produce completely different products. (Note that another good example is the reaction of methylbenzene with chlorine.) With dilute sodium hydroxide solution the OH^- ion acts as a nucleophile and substitution occurs to produce an alcohol, e.g.



However with hot alcoholic sodium hydroxide solution (i.e. sodium hydroxide dissolved in ethanol) **elimination** occurs and an alkene is formed, e.g.



In this reaction the hydroxide ion reacts as a base. The elimination of HBr can proceed either by a carbocation or as a concerted process, e.g.

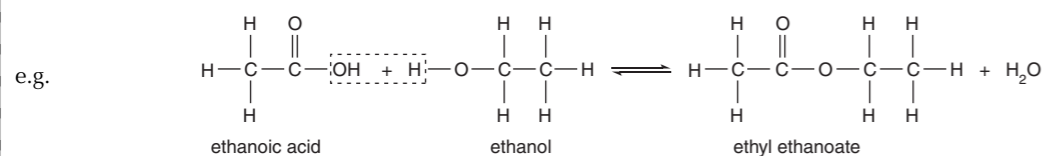


In the presence of ethanol there will also be some ethoxide ions present. Ethoxide is a stronger base than hydroxide so the equilibrium lies to the left but some ethoxide ions will be present and these may be the actual species acting as the base.



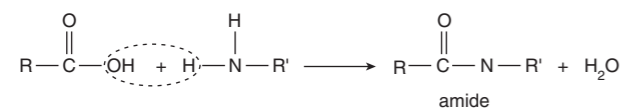
CONDENSATION REACTIONS

A condensation reaction involves the reaction between two molecules to produce a larger molecule with the elimination of a small molecule such as water or hydrogen chloride. One important condensation reaction is the formation of esters when an alcohol reacts with a carboxylic acid.



Most esters have a distinctive, pleasant, fruity smell and are used both as natural and artificial flavouring agents in food. For example, ethyl methanoate $\text{HCOOCH}_2\text{CH}_3$ is added to chocolate to give it the characteristic flavour of 'rum truffle'. Esters are also used as solvents in perfumes and as plasticizers (substances used to modify the properties of polymers by making them more flexible).

Another example of a condensation reaction is the formation of secondary amides by reacting a carboxylic acid with an amine.



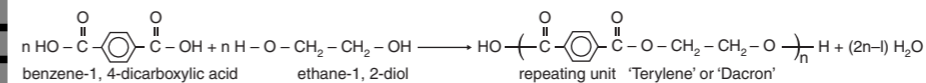
This reaction is important in biological reactions as amino acids contain an amine group and a carboxylic acid group so that amino acids can condense together in the presence of enzymes to form poly(amides).

Condensation polymerization and reaction pathways

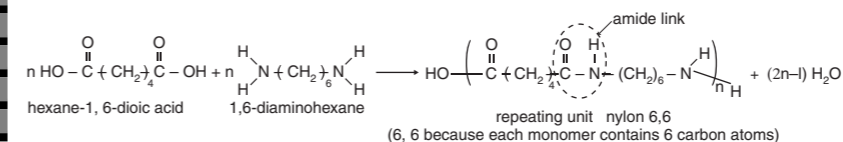
CONDENSATION POLYMERIZATION

Condensation involves the reaction between two molecules to eliminate a smaller molecule, such as water or hydrogen chloride. If each of the reacting molecules contain *two* functional groups that can undergo condensation, then the condensation can continue to form a polymer.

An example of a polyester is polyethene terephthalate (known as Terylene in the UK and as Dacron in the USA) used for textiles, which is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

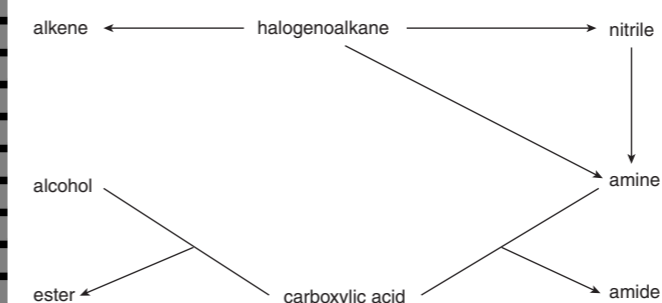


Amines can also condense with carboxylic acids to form an amide link (also known as a peptide bond). One of the best known examples of a polyamide is nylon.



REACTION PATHWAYS

The compounds and reaction types covered in the AHL can be summarized in the following scheme:

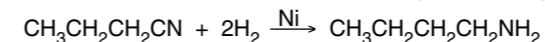


Given the starting materials, two step syntheses for new products can be devised. For example, the conversion of 1-bromopropane to 1-aminobutane (1-butylamine) can be performed in the following two stages.

Step 1. 1-bromopropane can undergo nucleophilic substitution with potassium cyanide solution to form propanenitrile.

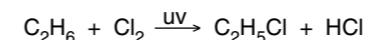


Step 2. Propanenitrile can be reduced by heating with hydrogen over a nickel catalyst.

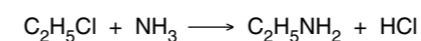


Another example would be the formation of ethylamine starting with ethane. Now reactions covered in the core can also be included.

Step 1. React ethane with chlorine in ultraviolet light so that chloroethane is formed by free radical substitution.



Step 2. React chloroethane with ammonia.

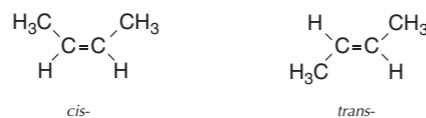


HL Stereoisomerism (1)

Structural isomers share the same molecular formula but have different structural formulas. That is, their atoms are bonded in different ways. Stereoisomers have the same structural formula but differ in their spatial arrangement. There are two types of stereoisomerism: geometrical isomerism and optical isomerism.

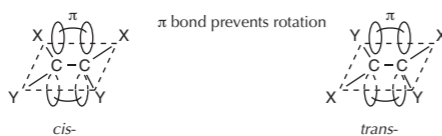
GEOMETRICAL ISOMERISM

Geometrical isomerism occurs when rotation about a bond is restricted or prevented. The classic examples of geometric isomers occur with asymmetric non-cyclic alkenes. A *cis*- isomer is one in which the substituents are on the same side of the double bond. In a *trans*- isomer the substituents are on opposite sides of the double bond. For example consider *cis*-but-2-ene and *trans*-but-2-ene.

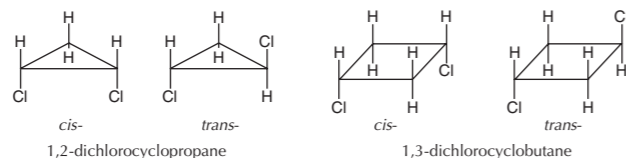


When there is a single bond between two carbon atoms free rotation about the bond is possible. However, the double bond in an alkene is made up of a σ and a π bond. The π bond is formed from the combination of two p orbitals, one from each of the carbon atoms. These two p orbitals must be in the same plane to combine. Rotating the bond would cause the π bond to break so no rotation is possible.

Cis- and *trans*- isomerism will always occur in alkenes when the two groups attached to each of the two carbon atoms are different.

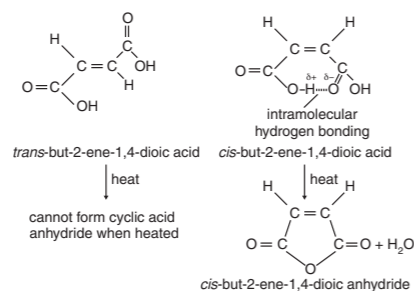


Geometrical isomerism can also occur in disubstituted cycloalkanes. The rotation is restricted because the C-C single bond is part of a ring system. Examples include 1,2-dichlorocyclopropane and 1,3-dichlorocyclobutane.



PHYSICAL AND CHEMICAL PROPERTIES OF GEOMETRICAL ISOMERS

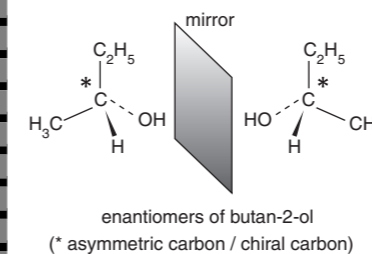
The chemical properties of geometric isomers tend to be similar but their physical properties are different. For example, the boiling point of *cis*-1,2-dichloroethene is 60.3 °C whereas *trans*-1,2-dichloroethene boils at the lower temperature of 47.5 °C. Sometimes there can be a marked difference in both chemical and physical properties. This tends to occur when there is some sort of chemical interaction between the substituents. *cis*-but-2-ene-1,4-dioic acid melts with decomposition at 130–131 °C. However, *trans*-but-2-ene-1,4-dioic acid does not melt until 286 °C. In the *cis*- isomer the two carboxylic acid groups are closer together so that intramolecular hydrogen bonding is possible between them. In the *trans*- isomer they are too far apart to attract each other so there are stronger intermolecular forces of attraction between different molecules, resulting in a higher melting point. The *cis*- isomer reacts when heated to lose water and form a cyclic acid anhydride. The *trans*- isomer cannot undergo this reaction.



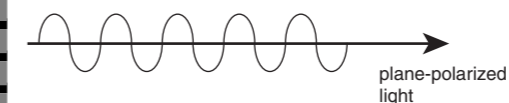
HL Stereoisomerism (2)

OPTICAL ISOMERISM

Optical isomerism is shown by all compounds that contain at least one asymmetric or chiral carbon atom within the molecule, that is, one that contains four different atoms or groups bonded to it. The two isomers are known as enantiomers and are mirror images of each other. Example include butan-2-ol, CH₃CH(OH)C₂H₅, 2-hydroxypropanoic acid (lactic acid), CH₃CH(OH)COOH and all amino acids (except glycine, NH₂CH₂COOH).



The two different isomers are optically active with plane-polarized light. Normal light consists of electromagnetic radiation which vibrates in all planes. When it is passed through a polarizing filter the waves only vibrate in one plane and the light is said to be plane-polarized.

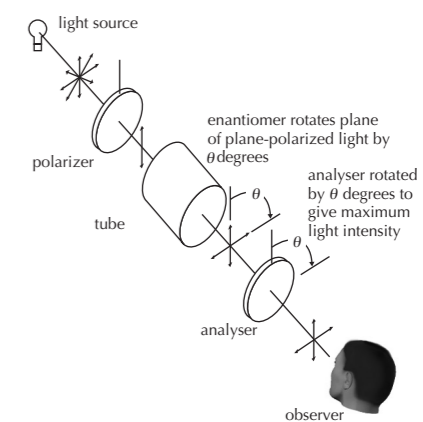


The two enantiomers both rotate the plane of plane-polarised light. One of the enantiomers rotates it to the left and the other rotates it by the same amount to the right. Apart from their behaviour towards plane-polarised light enantiomers have identical physical properties. Their chemical properties are identical too except when they interact with other optically active substances. This is often the case in the body where the different enantiomers can have completely different physiological effects. For example one of the enantiomers of the amino acid asparagine H₂NCH(CH₂CONH₂)COOH tastes bitter whereas the other enantiomer tastes sweet.

ENANTIOMERS

The optical activity of enantiomers can be detected and measured by an instrument called a polarimeter. It consists of a light source, two polarizing lenses, and between the lenses a tube to hold the sample of the enantiomer.

When light passes through the first polarizing lens (polarizer) it becomes plane-polarized. That is, it is vibrating in a single plane. With no sample present the observer will see the maximum intensity of light when the second polarizing lens (analyser) is in the same plane. Rotating the analyser by 90° will cut out all the light. When the sample is placed between the lenses the analyser must be rotated by θ degrees, either clockwise (dextrorotatory) or anticlockwise (laevorotatory) to give light of maximum intensity. The two enantiomers rotate the plane of plane-polarized light by the same amount but in opposite directions. If both enantiomers are present in equal amounts the two rotations cancel each other out and the mixture appears to be optically inactive. Such a mixture is known as a **racemic mixture** or **racemate**.



IB QUESTIONS – ORGANIC CHEMISTRY

1. Which of the following is/are true about alkanes?
- They form an homologous series with the general formula C_nH_{2n-2}
 - They all have identical physical properties
 - They all have similar chemical properties

A. I, II and III C. I and III only
 B. II and III only D. III only

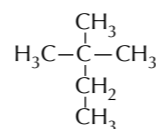
2. Which of the following two compounds both belong to the same homologous series?

A. CH_3COOH and $HCOOCH_3$
 B. CH_3OH and C_2H_5OH
 C. C_2H_4 and C_2H_6
 D. C_2H_5Cl and $C_2H_4Cl_2$

3. How many different isomers of C_5H_{12} exist?

A. 1 B. 2 C. 3 D. 4

4. Give the correct name for:



A. 2-methyl-2-ethylpropane C. 2,2-dimethylbutane
 B. hexane D. 2-methylpentane

5. Which statement is correct about the reaction between methane and chlorine?

A. It involves heterolytic fission and Cl^- ions.
 B. It involves heterolytic fission and $Cl\cdot$ radicals.
 C. It involves homolytic fission and Cl^- ions.
 D. It involves homolytic fission and $Cl\cdot$ radicals.



12. Identify which two compounds can react together to form a condensation polymer.

A. C_2H_4 and Br_2
 B. C_2H_5OH and CH_3COOH
 C. $H_2N(CH_2)_6NH_2$ and CH_3COOH
 D. $HOOC(CH_2)_4COOH$ and $HOCH_2CH_2OH$

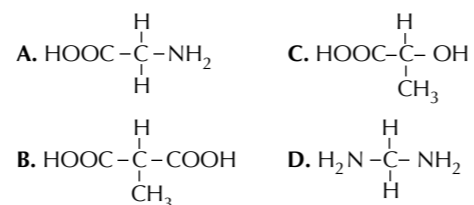
13. Consider the following reaction:



What will be the final product if aminoethane (ethylamine) is used instead of NH_3 ?

A. $CH_3CONHCH_2CH_3$ C. CH_3CONH_2
 B. $CH_3CONHCH_3$ D. $CH_3CONH_2CH_2CH_3$

14. Which compound can exhibit optical isomerism?



6. Which compound is an ester?

A. CH_3COOH C. C_2H_5CHO
 B. $CH_3OC_2H_5$ D. $HCOOCH_3$

7. When ethanol is partially oxidized by an acidified solution of potassium dichromate(VI), the product that can be obtained by distillation as soon as it is formed is:

A. ethanal C. ethanoic acid
 B. ethene D. ethane-1,2-diol

8. Which formula is that of a secondary halogenoalkane?

A. $CH_3CH_2CH_2CH_2Br$ C. $(CH_3)_2CHCH_2Br$
 B. $CH_3CHBrCH_2CH_3$ D. $(CH_3)_2CBr$

9. Which cannot undergo an addition reaction with ethene?

A. oxygen C. water
 B. hydrogen D. hydrogen bromide

10. Which compound is converted to butanal by acidified potassium dichromate(VI) solution?

A. butan-1-ol C. butanone
 B. butan-2-ol D. butanoic acid

11. Which reaction(s) involve(s) the formation of a positive ion?

I. $CH_3CH_2CH_2Br + OH^-$
 II. $(CH_3)_3CBr + OH^-$

A. I only C. Both I and II
 B. II only D. Neither I nor II

15. A ketone containing four carbon atoms will be formed from the reaction of an acidified solution of potassium dichromate(IV) solution with:

A. $CH_3CH_2CH_2CH_2OH$ C. $CH_3CH_2CH_2CHO$
 B. $(CH_3)_3COH$ D. $CH_3CH_2CH(OH)CH_3$

16. Which of the following will give an amine as the product?

I. $(CH_3)_3CBr + NH_3$ II. $CH_3CN + H_2$ III. $CH_3COOH + NH_3$

A. I, II and III C. I only
 B. I and II only D. I and III only

17. Which statement(s) is/are true about the reactions of halogenoalkanes with warm dilute sodium hydroxide solution

I. CH_3I reacts faster than CH_3F
 II. $(CH_3)_3CBr$ reacts faster than CH_3Br
 III. $(CH_3)_3CBr$ and $(CH_3)_3CCl$ both react by S_N1 mechanisms.

A. I and II only C. II and III only
 B. I, II and III D. I only