10 ORGANIC CHEMISTRY

Fundamentals of organic chemistry

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**

hydroxyl: –OH = **-ol**

amino: $-NH_2$ = **amino-**

halo: –X: **chloro-**, **bromo-** or **iodo-**

aldehyde: $-\overset{\overset{O}{\|}}{C}-H$ (on the end of the chain) = **-al**

ketone: $-\overset{\overset{O}{\|}}{C}-$(not on the end of the chain) = **-one**

carboxyl: $-\overset{\overset{O}{\|}}{C}-OH$ = **-oic acid**

ester: $-\overset{\overset{O}{\|}}{C}-OR$: = **-oate**

4. Numbers are used to give the position 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 CH_4

ethane C_2H_6

propane C_3H_8

butane C_4H_{10}

If one of the hydrogen atoms is removed what is left is known as an alkyl radical R – (e.g methyl CH_3–; ethyl C_2H_5–). 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 $-CH_2-$; for example the general formula of alcohols is $C_nH_{2n+1}OH$. The chemical properties of the individual members of a homologous series are similar and they show a gradual change in physical properties.

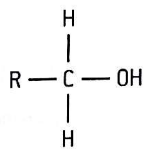
CLASS OF ORGANIC COMPOUND

Different compounds that all contain the same functional group are divided into classes. Sometimes the name of the class is the same as the functional group, but sometimes it is different. For example, the name of the class is the same for all **esters** that contain the **ester functional group**, (**–COOR**), but it is different for all **alcohols** that contain the **hydroxyl**, (**–OH**), **functional group**. The carbonyl functional group is –CO– where the carbon atom is joined by a double bond to the oxygen atom. Several classes of compounds contain this functional group as it depends upon what else is bonded to the carbon atom. For example, if H is bonded to the carbon atom then they are known as aldehydes (–COH), whereas if an alkyl group is bonded to the carbon atom then they are known as ketones (–COR). The –COOH functional group is known as the carboxyl group and the class of compounds containing this group is called carboxylic acids. Compounds containing an amino group are known as amines and compounds containing a halo group are known as halogenoalkanes (or more specifically chloroalkanes, bromoalkanes or iodoalkanes).

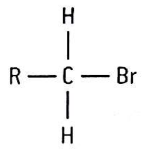
CLASSIFICATION OF ALCOHOLS, HALOGENOALKANES AND AMINES

Alcohols and halogenoalkanes may be classified according to how many –R groups are bonded to the carbon atom containing the functional group. Similar logic applies to amines but now it is the number of –R groups attached to the nitrogen atom of the amino functional group.

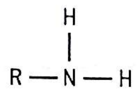
primary (one –R group bonded to the C or N atom)



$R-\underset{H}{\overset{H}{C}}-OH$



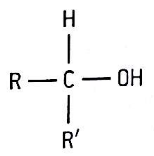
$R-\underset{H}{\overset{H}{C}}-Br$



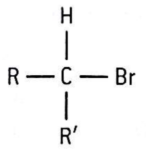
$R-\overset{H}{N}-H$

secondary (two –R groups bonded to the C or N atom)

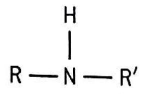
R′ may be the same as R or different



$R-\underset{R'}{\overset{H}{C}}-OH$

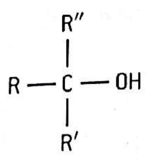


$R-\underset{R'}{\overset{H}{C}}-Br$

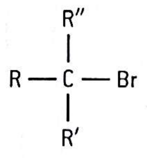


$R-\overset{H}{N}-R'$

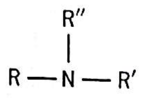
tertiary (three –R groups bonded to the C or N atom)



$R-\underset{R'}{\overset{R''}{C}}-OH$



$R-\underset{R'}{\overset{R''}{C}}-Br$

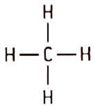
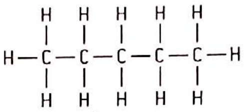
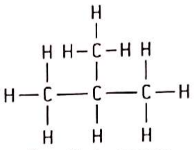
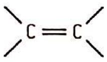
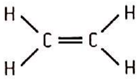
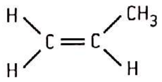
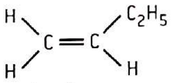
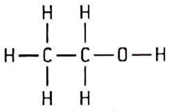
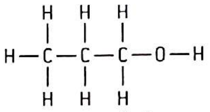
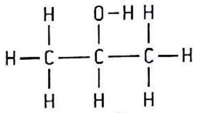
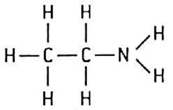
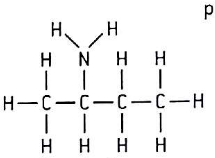
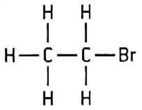
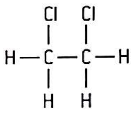
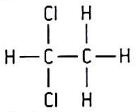
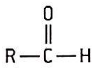
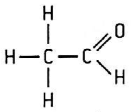
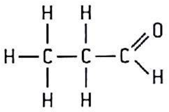
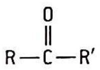
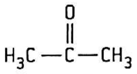
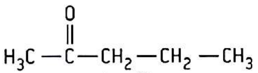
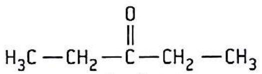
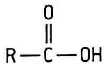
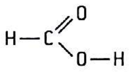
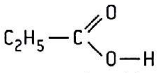
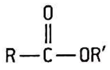
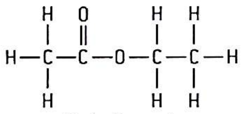
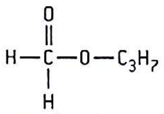
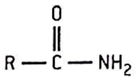
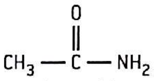
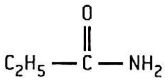
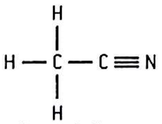
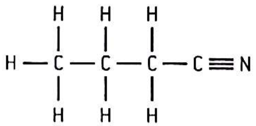
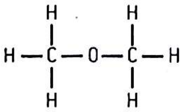
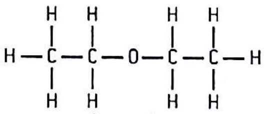
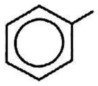
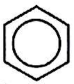
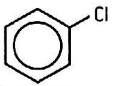
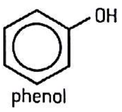


$R-\overset{R''}{N}-R'$

R″ may be the same as R′ or R or may be different.

Common classes of organic compounds

SOME COMMON CLASSES OF ORGANIC COMPOUNDS

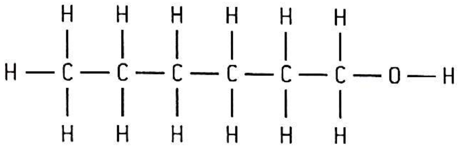
Formula	Name	Examples
R—H	alkane	 methane  butane  2-methylpropane
	alkene functional group: alkenyl	 ethene  propene  but-1-ene
—C≡C—	alkyne functional group: alkynyl	H—C≡C—H ethyne H—C≡C—CH_3 propyne
R—OH	alcohol functional group: hydroxy	 ethanol  propan-1-ol  propan-2-ol
R—NH_2	amine	 ethylamine (aminoethane)  2-aminobutane
R—X (X = F, Cl, Br, or I)	halogenoalkane	 bromoethane  1, 2-dichloroethane  1, 1-dichloroethane
 $R-\overset{\overset{O}{\|}}{C}-H$	aldehyde	 ethanal  propanal
 $R-\overset{\overset{O}{\|}}{C}-R'$	ketone (R′ may be the same as or different to R)	 $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$ propanone  $H_3C-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$ pentan-2-one  $H_3C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ pentan-3-one
 $R-\overset{\overset{O}{\|}}{C}-OH$	carboxylic acid	 methanoic acid  propanoic acid
 $R-\overset{\overset{O}{\|}}{C}-OR'$	ester	 ethyl ethanoate  propyl methanoate
 $R-\overset{\overset{O}{\|}}{C}-NH_2$	carboxamide	 $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ ethanamide  $C_2H_5-\overset{\overset{O}{\|}}{C}-NH_2$ propanamide
R—C≡N	nitrile	 ethanenitrile  butanenitrile
R—O—R′	ether	 methoxymethane  ethoxyethane
	(C_6H_5–) benzene ring functional group: phenyl	 benzene  chlorobenzene  phenol

Structural formulas

STRUCTURAL FORMULAS

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

These may be shown in a variety of different ways but all ways should show unambiguously how the atoms are bonded together. When drawing full structural formulas with lines representing bonds and the symbol of the element representing atoms, all the hydrogen atoms must also be included in the diagram. This is because the skeletal formula does not include any symbols for the elements and the end of a line represents a methyl group unless another atom is shown attached. Although you should understand skeletal formulas they are not normally used for simple formulas except where benzene is involved. Note that unless specifically asked for, 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. $CH_3CH_2CH_2CH_2CH_3$ or $CH_3–(CH_2)_3–CH_3$ for pentane but the molecular formula, C_5H_{12} will not suffice.

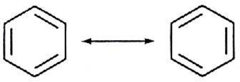


Structural formula of hexan-1-ol
also acceptable are
$CH_3CH_2CH_2CH_2CH_2CH_2OH$
and $CH_3(CH_2)_4CH_2OH$

skeletal formula of hexan-1-ol

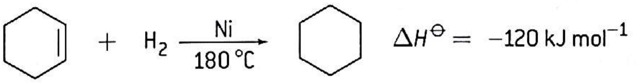
STRUCTURAL FORMULA OF BENZENE

The simplest aromatic compound (arene) is benzene, C_6H_6. The Kekulé structure of benzene (cyclohexa-1,3,5-triene) consists of three double bonds.



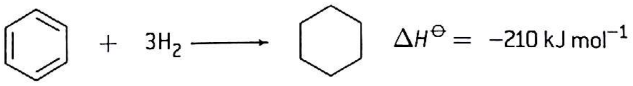
There is both physical and chemical evidence to support the fact that benzene does not contain three separate double bonds but exists as a resonance hybrid structure with delocalized electrons. The two resonance hybrid forms are shown (right).

1. The C–C bond lengths are all the same and have a value of 0.140 nm which lies between the values for C–C (0.154 nm) and C=C (0.134 nm).
2. The enthalpy of hydrogenation of cyclohexene is –120 kJ mol⁻¹.



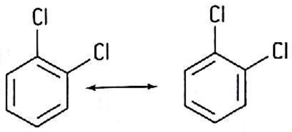
If benzene simply had the cyclohexa-1,3,5-triene structure with three double bonds the enthalpy change of hydrogenation of benzene would be expected to be equal to 3 times the enthalpy change of hydrogenation of cyclohexene, i.e. –360 kJ mol⁻¹.

However the experimentally determined value for benzene is –210 kJ mol⁻¹.



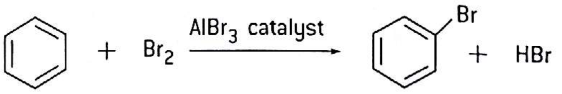
The difference of 150 kJ mol⁻¹ is the extra energy associated with the delocalization.

3. Only one isomer exists for 1,2- disubstituted benzene compounds. If there were simply alternate double bonds then two isomers would exist.

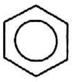


The two isomers of 1, 2- dichlorobenzene which would be expected if benzene has the cyclohexa-1, 3, 5-triene structure

4. If benzene had three normal double bonds it would be expected to readily undergo addition reactions. In fact it will only undergo addition reactions with difficulty and more commonly undergoes substitution reactions. For example, with bromine it forms bromobenzene and hydrogen bromide rather than 1,2-dibromobenzene.



The actual bonding in benzene is best described by the delocalization of electrons. For this reason benzene is often represented by a hexagonal ring with a circle in the middle of it.

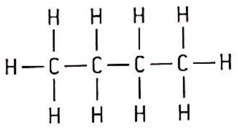


Structural isomers

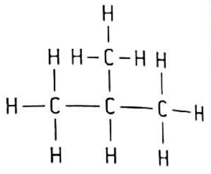
STRUCTURAL FORMULAS OF HYDROCARBONS

Isomers of alkanes

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

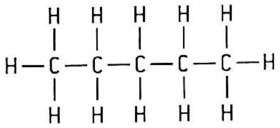


butane

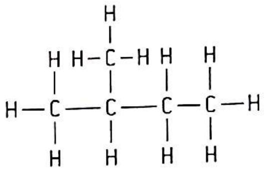


2-methylpropane

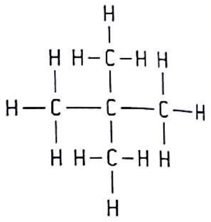
These are examples of structural isomers. **Structural isomers** have the same molecular formula but a different structural formula. They normally have similar chemical properties but their physical properties may be slightly different. There are three structural isomers of pentane.



pentane



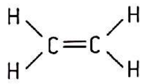
2-methylbutane



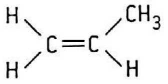
2, 2-dimethylpropane

Isomers of alkenes and alkynes

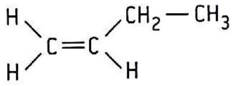
Alkenes and alkynes are unsaturated. The alkenes ethene and propene each have only one possible structure but butene has three structural isomers. Similarly the alkynes ethyne and propyne each have only one possible structure but butyne has two.



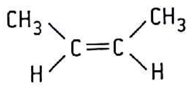
ethene



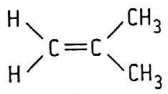
propene



but-1-ene



but-2-ene



2-methylpropene

$H-C\equiv C-H$

ethyne

$H-C\equiv C-CH_3$

propyne

$H-C\equiv C-CH_2-CH_3$

but-1-yne

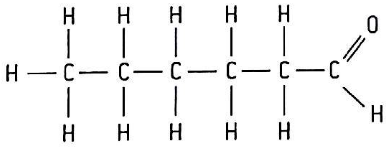
$CH_3-C\equiv C-CH_3$

but-2-yne

NAMING STRUCTURAL ISOMERS

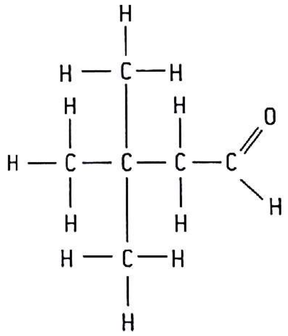
The naming system explained on page 79 is known as the IUPAC (International Union of Pure and Applied Chemistry) system. The IUPAC names to distinguish between structural isomers of alkanes, alkenes, alkynes, alcohols, ethers, halogenoalkanes, aldehydes, ketones, esters and carboxylic acids, each containing up to six carbon atoms, are required.

For example, four different structural isomers with the molecular formula $C_6H_{12}O$ are shown.



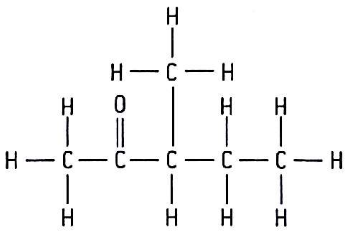
or $CH_3CH_2CH_2CH_2CH_2CHO$

hexanal



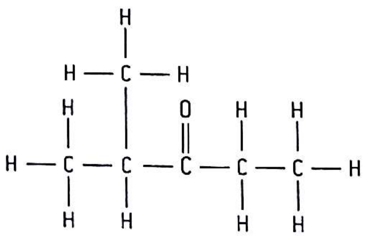
$CH_3C(CH_3)_2CH_2CHO$

3, 3-dimethylbutanal



or $CH_3COCH(CH_3)CH_2CH_3$

3-methylpentan-2-one



or $CH_3CH(CH_3)COCH_2CH_3$

2-methylpentan-3-one

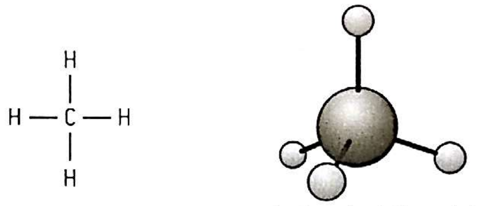
3-D models of structural formulas

3-D REPRESENTATIONS

To help distinguish between isomers and because the chemical and physical properties of molecules depend upon their shape and the types of bonds and functional groups they contain it is helpful to be able to visualize the structures in three dimensions. Two-dimensional display diagrams of alkanes, for examples, wrongly suggest that the H–C–H bond angles are 90° instead of 109.5°. The traditional way in which chemists have approached this is to use a full 'wedge' to show an atom coming out of the two dimensional page and a dotted line to show it going behind the page.

The very best way to 'see' molecular structures in three dimensions is to use a molecular modelling kit and build the models for yourself. This can be particularly helpful when distinguishing between isomers and understanding bond angles. Two common ways to represent molecules in 3-D are 'ball and stick' models or space-fill models. You can also see virtual 3-D representations using apps on your laptop, smart phone or tablet, which are also able to show the molecules rotating. However it is easy to forget that these are still being displayed on a 2-D screen so are not truly three dimensional.

Some models of the structure of methane



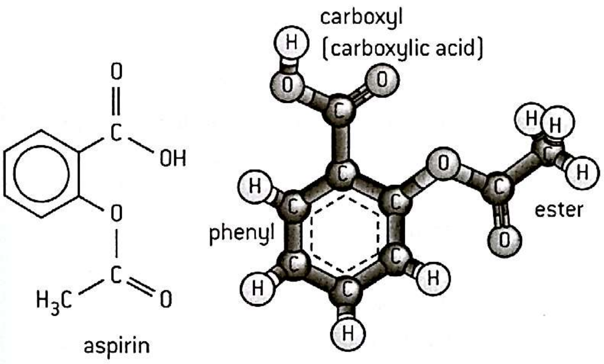
traditional 2-D 'display'   'ball and stick' model

traditional 3-D representation   'space-fill' model

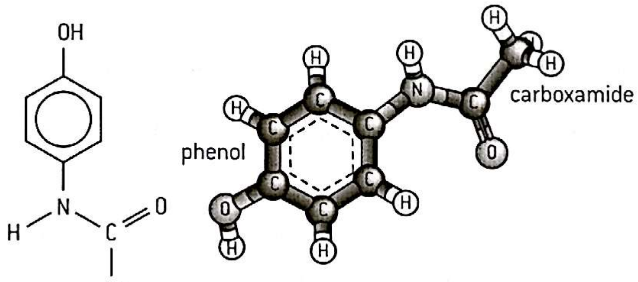
IDENTIFYING FUNCTIONAL GROUPS IN MOLECULES FROM VIRTUAL 3-D MODELS

As well as recognizing different functional groups within more complex molecules from their structural formulas you should also be able to recognize them from virtual 3-D representations.

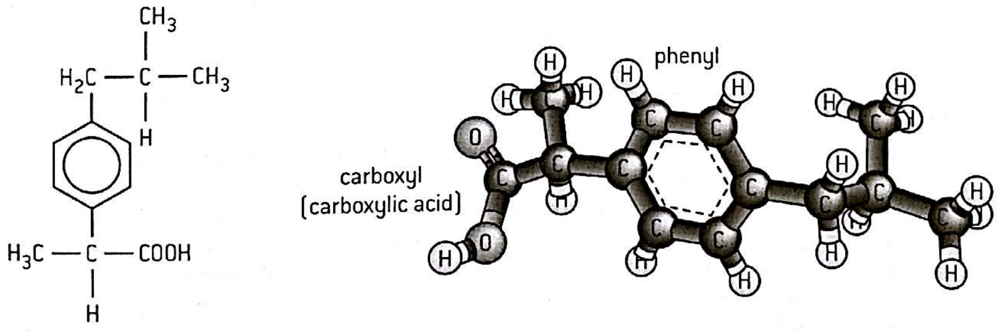
The following three molecules, aspirin, paracetamol (acetaminophen) and ibuprofen, are all mild pain killers. As you can see they all contain a phenyl group, although this is a phenol in paracetamol as the phenyl group is directly bonded to an hydroxyl group. Aspirin and ibuprofen contain a carboxyl group (carboxylic acid), aspirin also contains an ester group and paracetamol contains a carboxamide group. If you look at past papers or in the IB data booklet you can find other molecules such as morphine and heroin where you can do a similar exercise.



aspirin



paracetamol (acetaminophen)



Ibuprofen

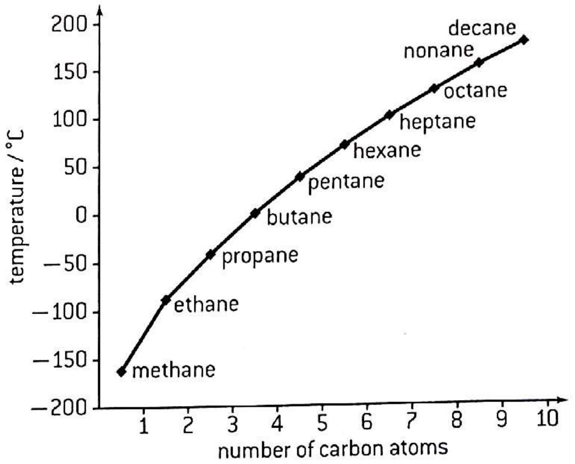
Properties of different homologous series

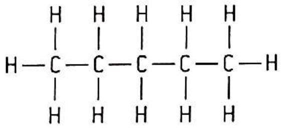
BOILING POINTS

As the carbon chain in the homologous series of alkanes increases the London dispersion forces of attraction increase and hence the boiling point also increases. A plot of boiling points against number of carbon atoms shows a sharp increase at first, as the percentage increase in mass is high, but as successive $-CH_2-$ groups are added the rate of increase in boiling point decreases.

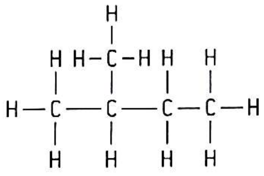
When branching occurs the molecules become more spherical in shape, which reduces the contact surface area between them and lowers the boiling point.

Boiling points of the alkanes

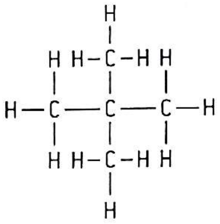




pentane
(b. pt 36.3 °C)



2-methylbutane
(b. pt 27.9 °C)



2, 2-dimethylpropane
(b. pt 9.5 °C)

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	Mr	Class of compound	Strongest type of attraction	B. pt / °C
butane	C_4H_{10}	58	alkane	London dispersion forces	−0.5
but-1-ene	C_4H_8	56	alkene	London dispersion forces	−6.5
but-1-yne	C_4H_6	54	alkyne	London dispersion forces	8.1
methyl methanoate	$HCOOCH_3$	60	ester	dipole–dipole	31.5
propanal	CH_3CH_2CHO	58	aldehyde	dipole–dipole	48.8
propanone	CH_3COCH_3	58	ketone	dipole–dipole	56.2
aminopropane	$CH_3CH_2CH_2NH_2$	59	amine	hydrogen bonding	48.6
propan-1-ol	$CH_3CH_2CH_2OH$	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.

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:

$$C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

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)

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ \Delta H^\ominus = -890.4\ \text{kJ mol}^{-1}$$

gasoline (petrol)

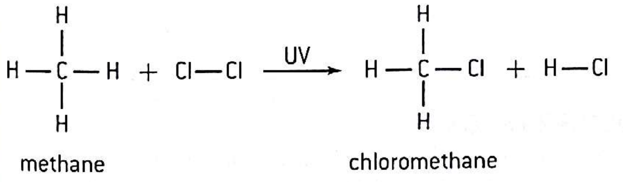
$$C_8H_{18}(l) + 12\tfrac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$$

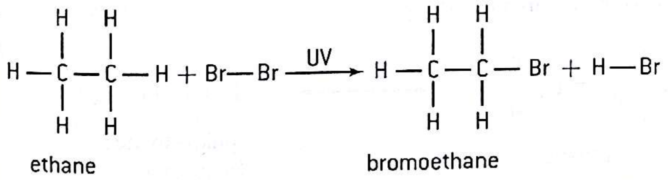
$$\Delta H^\ominus = -5512\ \text{kJ mol}^{-1}$$

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.

$$Cl_2 \rightarrow Cl^\bullet + Cl^\bullet$$

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.

$$H_3C{-}H + Cl^\bullet \rightarrow H_3C^\bullet + HCl$$

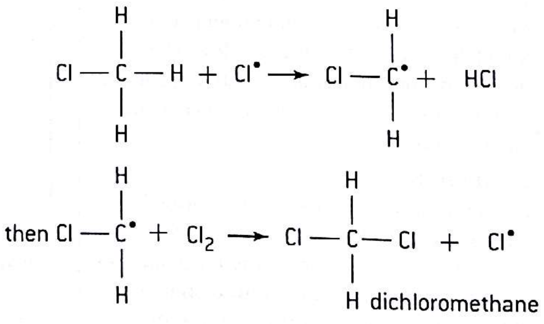
Since a new radical is produced this stage of the mechanism is called **propagation**. The methyl free radical is also extremely reactive and reacts with a chlorine molecule to form the product and regenerate another chlorine radical. This is a further propagation step and enables a chain reaction to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

$$CH_3^\bullet + Cl_2 \rightarrow CH_3{-}Cl + Cl^\bullet$$

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.

$$\left.\begin{array}{l} Cl^\bullet + Cl^\bullet \rightarrow Cl_2 \\ CH_3^\bullet + Cl^\bullet \rightarrow CH_3Cl \\ CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6 \end{array}\right\} \quad \text{termination}$$

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



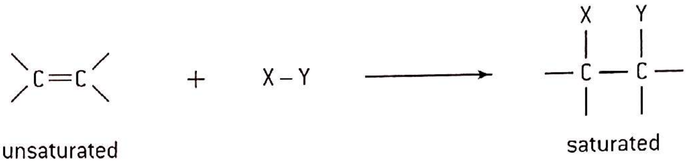
The substitution can continue even further to produce trichloromethane and then tetrachloromethane.

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

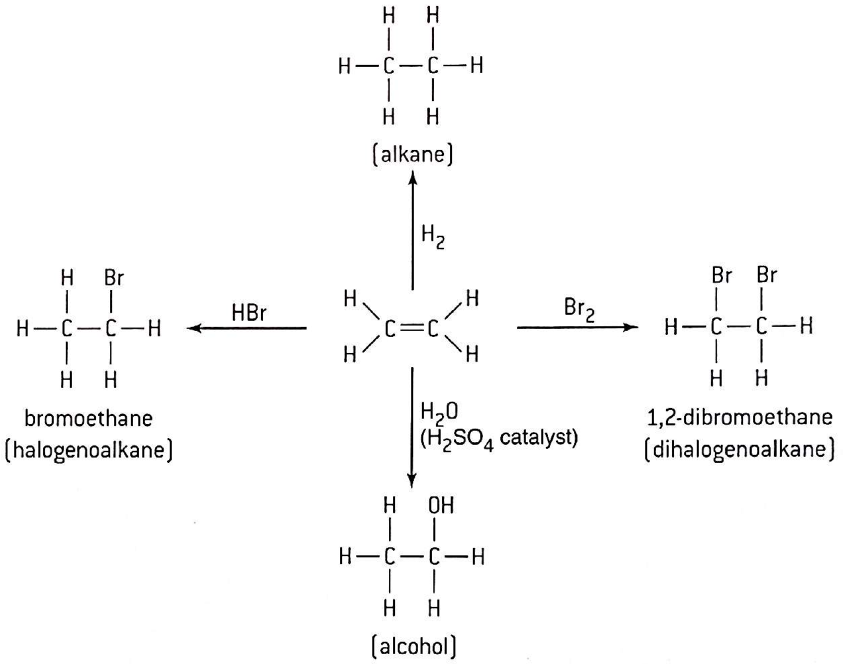
Alkenes

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 348kJ 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 decolourization of bromine solution provides a useful test to indicate the presence of an alkene group.

2. **Hydration**

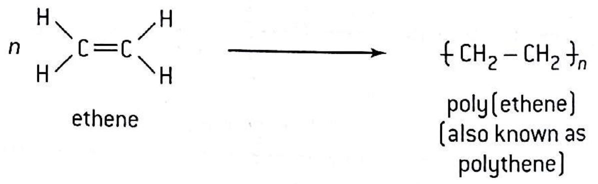
Ethene is an important product formed during the cracking of oil. Although ethanol can be made from the fermentation of starch and sugars, much industrial ethanol is formed from the addition of steam to ethene.

3. **Hydrogenation**

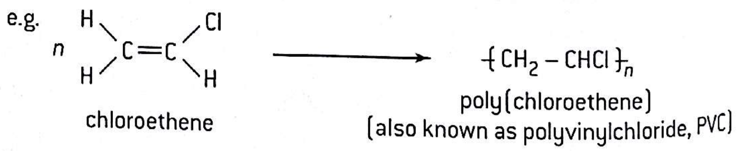
The addition of hydrogen to unsaturated vegetable oils is used industrially to make margarine. Hydrogenation reduces the number of double bonds in the polyunsaturated vegetable oils present in the margarine, which causes it to become a solid at room temperature.

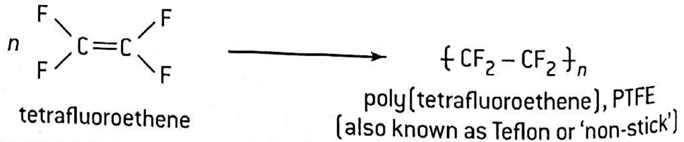
ADDITION POLYMERIZATION

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.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^{\ominus} = -1371 \text{ kJ mol}^{-1}$$

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:

$$C_nH_{(2n+1)}OH + (2n-1)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

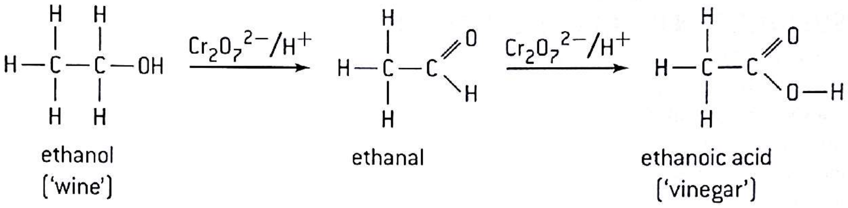
OXIDATION OF ETHANOL

Ethanol can be readily oxidized by warming with an acidified solution of potassium dichromate(VI). During the process the orange dichromate(VI) ion $Cr_2O_7^{2-}$ 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.

$$3CH_3CH_2OH(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CHO(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

The ethanal is then oxidized further to ethanoic acid.



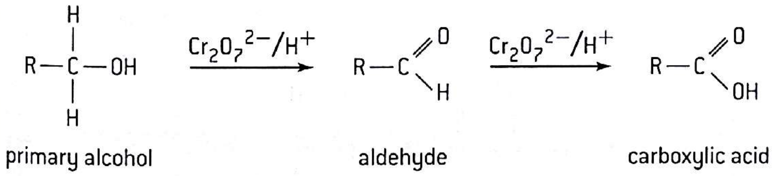
$$3CH_3CHO(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3COOH(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$$

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.

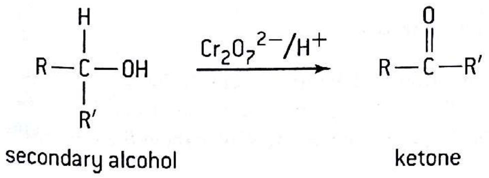
OXIDATION OF ALCOHOLS

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.

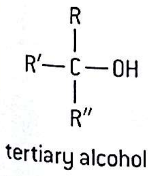
All **primary alcohols** are oxidized by acidified potassium dichromate(VI), first to aldehydes then to carboxylic acids.



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



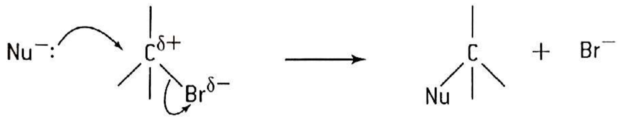
Tertiary alcohols cannot be oxidized by acidified dichromate(VI) ions as they have no hydrogen atoms attached directly to the carbon atom containing the –OH group. It is not true to say that tertiary alcohols can never be oxidized, as they burn readily, but when this happens the carbon chain is destroyed.



Substitution and condensation reactions

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 electron-deficient 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.

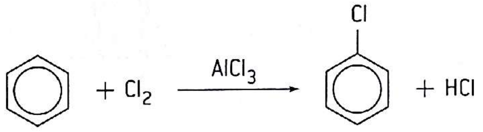
These reactions are useful in organic synthesis as a wide variety of different compounds can be made by varying the nucleophile. For example, with warm dilute sodium hydroxide solution the product is an alcohol, with ammonia the product is an amine and with cyanide ions, CN^-, the product is a nitrile. This last reaction is particularly useful as it provides a way to increase the number of atoms in the carbon chain.

Reaction of bromoethane with warm dilute sodium hydroxide solution:

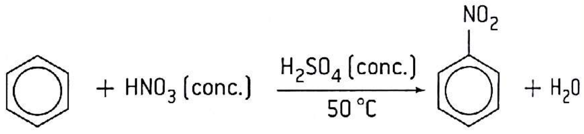
$$C_2H_5Br(l) + NaOH(aq) \rightarrow C_2H_5OH(aq) + NaBr(aq)$$

SUBSTITUTION REACTIONS OF BENZENE

The extra stability provided by the delocalization of the electrons in the benzene ring means that benzene, unlike simple alkenes, does not readily undergo addition reactions. However benzene does undergo substitution reactions. Benzene has a high electron density so reacts with electrophiles. Electrophiles are electron-deficient species often formed *in situ* that can accept electron pairs. Two examples of electrophilic substitution reactions of benzene are the reaction with chlorine in the presence of aluminium chloride (the electrophile is Cl^+) to form chlorobenzene and the reaction with nitric acid in the presence of sulfuric acid (the electrophile is NO_2^+) to form nitrobenzene.



chlorobenzene



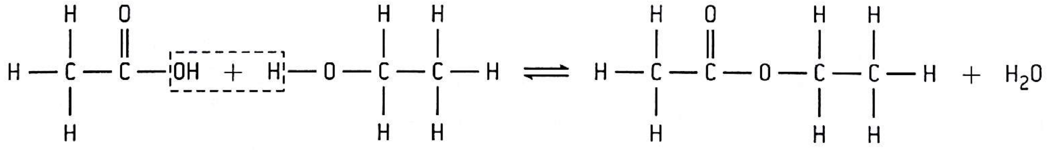
nitrobenzene

CONDENSATION REACTION BETWEEN AN ALCOHOL AND A CARBOXYLIC ACID

Alcohols can undergo a nucleophilic substitution reaction with carboxylic acids but this is more normally called esterification and is an example of a condensation reaction. 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.

Alcohols react with carboxylic acids in the presence of a small amount of concentrated sulfuric acid, which acts as a catalyst, to form an ester.

e.g.



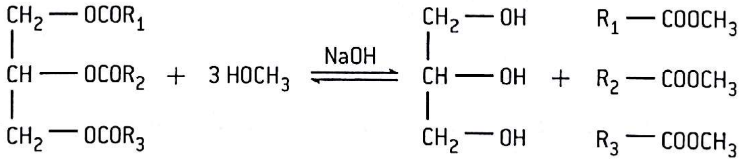
$$CH_3COOH + HOCH_2CH_3 \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

ethanoic acid ethanol ethyl ethanoate

Most esters have a distinctive, pleasant fruity smell and are used both as natural and artificial flavouring agents in food. For example, ethyl methanoate $HCOOCH_2CH_3$ 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.)

Many drugs contain one or more ester groups e.g. aspirin and heroin.

Fats and oils are natural triesters formed from the reaction between glycerol (propane-1,2-3-triol) and three fatty acids. In a process known as transesterification they can react with alcohols in the presence of sodium hydroxide (which acts as a catalyst) to form alkyl esters, which can be used as biofuel.



triglyceride (fat or oil) methanol glycerol methyl esters (biofuel)

HL Nucleophilic substitution

MECHANISM OF NUCLEOPHILIC SUBSTITUTION

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

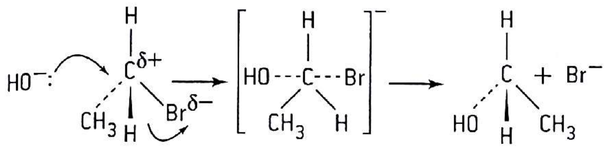
For example, the reaction between bromoethane and warm dilute sodium hydroxide solution.

$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$

The experimentally determined rate expression is:

rate = $k[C_2H_5Br][OH^-]$

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 S_N2 mechanism (bimolecular nucleophilic substitution).

Note that the S_N2 mechanism is stereospecific with an inversion of configuration at the central carbon atom.

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

For example, the reaction between 2-bromo-2-methylpropane and warm dilute sodium hydroxide solution.

$$C(CH_3)_3Br + OH^- \longrightarrow C(CH_3)_3OH + Br^-$$

The experimentally determined rate expression for this reaction is: rate = $k[C(CH_3)_3Br]$

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

$$C(CH_3)_3Br \xrightarrow{\text{slow}} C(CH_3)_3^+ + Br^-$$

$$C(CH_3)_3^+ + OH^- \xrightarrow{\text{fast}} C(CH_3)_3OH$$

In this reaction it is the first step, the heterolytic fission of the C–Br bond, that is the rate-determining step. The molecularity of this step is one and the mechanism is known as S_N1 (unimolecular nucleophilic substitution).

The mechanism for the hydrolysis of secondary halogenoalkanes (e.g 2-bromopropane $CH_3CHBrCH_3$) is more complicated as they can proceed by either S_N1 or S_N2 pathways or a combination of both.

CHOICE OF SOLVENT

Whether or not the reaction proceeds by an S_N1 or S_N2 mechanism also depends upon the solvent. Protic solvents which are polar, such as water or ethanol, favour the S_N1 mechanism as they support the breakdown of halogenoalkanes into carbocations and halide ions whereas aprotic solvents which are less polar such as ethoxyethane, $C_2H_5OC_2O_5$, favour an S_N2 mechanism involving a transition state.

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. This explains why the hydroxide ion is a much better nucleophile than water.

The nature of the halogen

For both S_N1 and S_N2 reactions iodoalkanes react faster than bromoalkanes, which in turn react faster than chloroalkanes. This is due to the relative bond enthalpies 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	228
C–Br	285
C–Cl	324

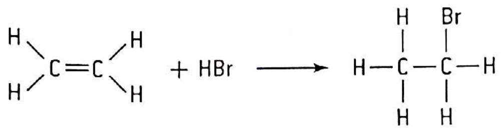
The nature of the halogenoalakane

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.

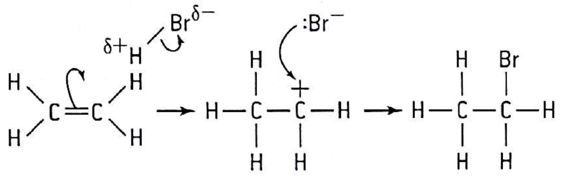
Electrophilic addition reactions (1)

ELECTROPHILIC ADDITION TO SYMMETRIC ALKENES

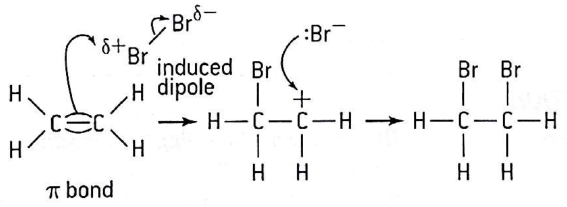
Ethene readily undergoes addition reactions. With hydrogen bromide it forms bromoethane.



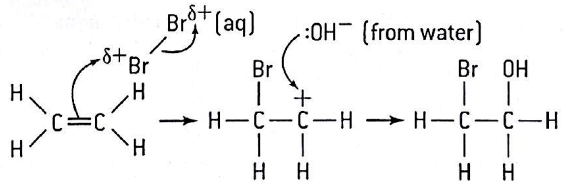
The reaction can occur in the dark which suggests that a free radical mechanism is not involved. The double bond in the ethene molecule has a region of high electron density above and below the plane of the molecule. Hydrogen bromide is a polar molecule due to the greater electronegativity of bromine compared with hydrogen. The hydrogen atom (which contains a charge of $\delta+$) from the H–Br is attracted to the double bond and the H–Br bond breaks, forming a bromide ion. At the same time the hydrogen atom adds to one of the ethene carbon atoms leaving the other carbon atom with a positive charge. A carbon atom with a positive charge is known as a **carbocation**. The carbocation then combines with the bromide ion to form bromoethane. Because the hydrogen bromide molecule is attracted to a region of electron density it is described as an **electrophile** and the mechanism is described as **electrophilic addition**.



Electrophilic addition also takes place when bromine adds to ethene in a non-polar solvent to give 1,2-dibromoethane. Bromine itself is non-polar but as it approaches the double bond of the ethene an induced dipole is formed by the electron cloud.



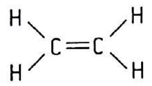
Evidence for this mechanism is that when bromine water is reacted with ethene the main product is 2-bromoethanol not 1,2-dibromoethane. This suggests that hydroxide ions from the water add to the carbocation in preference to bromide ions.

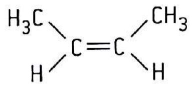


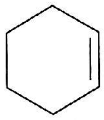
SYMMETRIC AND ASYMMETRIC ALKENES

Asymmetric alkenes contain different groups attached to the carbon atoms of the C=C bond.

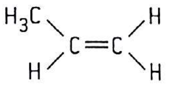
Symmetric alkenes

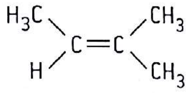

ethene

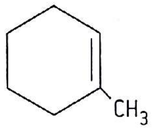

but-2-ene


cyclohexene

Asymmetric alkenes

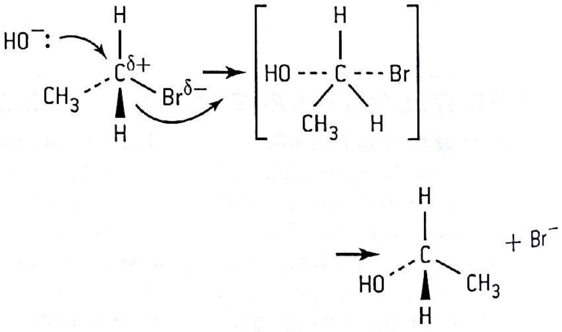

propene


2-methylbut-2-ene

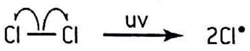

1-methylcyclohexene

CURLY ARROWS AND 'FISH HOOKS'

Curly arrows are used to show the movement of a pair of electrons as for example in the electrophilic addition reaction of hydrogen bromide with ethene shown in the opposite box. The 'tail' of the arrows shows the origin of the electron pair and the 'head' where the electron pair ends up. In S_N2 reactions such as the nucleophilic substitution reaction of bromoethane by hydroxide ions it is best to use three-dimensional representations to clarify the stereochemistry as the arrow head should go to the opposite side of the δ^+ carbon atom formed due to the polar C–Br bond (see page 89).



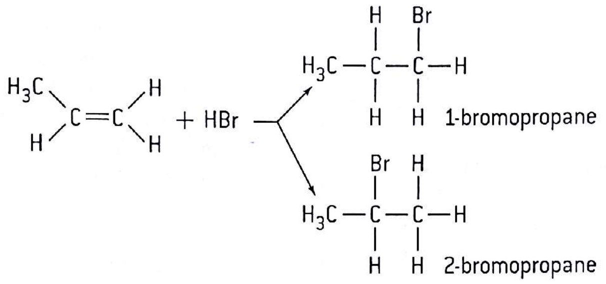
When single electrons are transferred as in the free radical substitution reactions of alkanes with halogens in ultraviolet light as described on page 85 then single-headed arrows known as 'fish hooks' are used. Thus the initiation step which involves the homolytic fission of the chlorine to chlorine bond by ultraviolet light can be represented as:



Electrophilic addition reactions (2)

MARKOVNIKOV'S RULE

When hydrogen halides add to asymmetric alkenes two products are possible depending upon which carbon atom the hydrogen atom bonds to. For example, the addition of hydrogen bromide to propene could produce 1-bromopropane or 2-bromopropane.

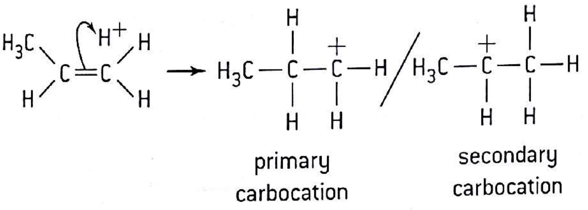


Markovnikov's rule enables you to predict which isomer will be the major product. It states that the hydrogen halide will add to the carbon atom that already contains the most hydrogen atoms bonded to it. Thus in the above example 2-bromopropane will be the major product.

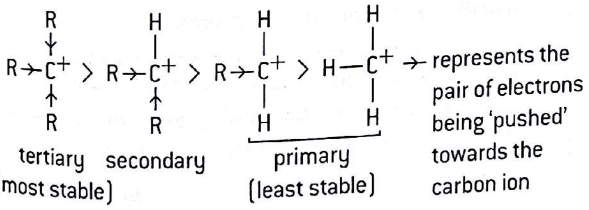
EXPLANATION OF MARKOVNIKOV'S RULE

Markovnikov's rule enables the product to be predicted but it does not explain why. It can be explained by considering the nature of the possible intermediate carbocations formed during the reaction.

When hydrogen ions react with propene two different carbocation intermediates can be formed.

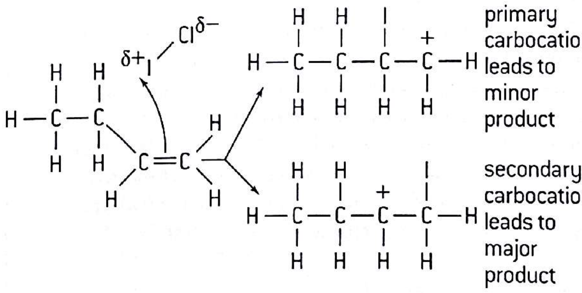


The first one has the general formula RCH_2^+ and is known as a **primary carbocation**. The second one has two R– groups attached to the positive carbon ion R_2CH^+ and is known as a **secondary carbocation**. A **tertiary carbocation** has the general formula R_3C^+. The R-groups (alkyl groups) tend to push electrons towards the carbon atom they are attached to which tends to stabilize the positive charge on the carbocation. This is known as a **positive inductive effect**. This effect will be greatest with tertiary carbocations and smallest with primary carbocations.



Thus in the above reaction the secondary carbocation will be preferred as it is more stable than the primary carbocation. This secondary carbocation intermediate leads to the major product, 2-bromopropane.

Understanding this mechanism enables you to predict what will happen when an interhalogen adds to an asymmetric alkene even though no hydrogen atoms are involved. Consider the reaction of iodine chloride ICl with but-1-ene. Since iodine is less electronegative than chlorine the iodine atom will act as the electrophile and add first to the alkene.

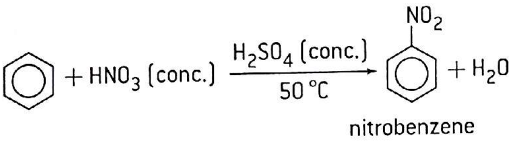


The major product will thus be 2-chloro-1-iodobutane.

HL Electrophilic substitution reactions and reduction reaction

NITRATION OF BENZENE

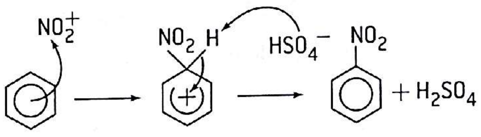
Benzene reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid when warmed at 50 °C to give nitrobenzene and water. Note that the temperature should not be raised above 50 °C otherwise further nitration to dinitrobenzene will occur.



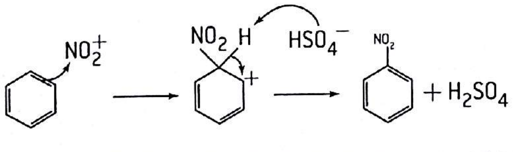
The electrophile is the **nitryl cation** NO_2^+ (also called the nitronium ion). The concentrated sulfuric acid acts as a catalyst. Its function is to protonate the nitric acid which then loses water to form the electrophile. In this reaction nitric acid is acting as a base in the presence of the more acidic sulfuric acid.

$$\begin{array}{c} H_2SO_4 + HNO_3 \rightleftharpoons H_2NO_3^+ + HSO_4^- \\ \downarrow \\ H_2O + NO_2^+ \end{array}$$

The NO_2^+ is attracted to the delocalized π bond and attaches to one of the carbon atoms. This requires considerable activation energy as the delocalized π bond is partially broken. The positive charge is distributed over the remains of the π bond in the intermediate. The intermediate then loses a proton and energy is evolved as the delocalized π bond is reformed. The proton can recombine with the hydrogensulfate ion to regenerate the catalyst.



Although it is more correct to draw the intermediate as a partially delocalized π bond it can sometimes be convenient to show benzene as if it does contain alternate single and double carbon to carbon bonds. In this model the positive charge is located on a particular carbon atom.



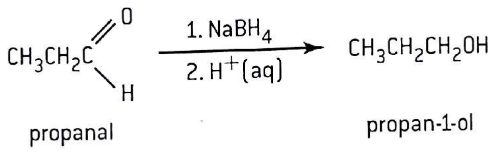
REDUCTION REACTIONS

a) Reduction of carbonyl compounds

There are several reducing agents that can be used to reduce carbonyl compounds. Typical among these are lithium tetrahydridoaluminate (also known as lithium aluminium hydride), $LiAlH_4$, and sodium tetrahydridoborate (also known as sodium borohydride), $NaBH_4$. Both effectively provide a source of H^- ions, which act as the reducing agent undergoing a nucleophilic addition reaction with the electron-deficient carbon atom of the carbonyl group. Sodium tetrahydridoborate can be used in the presence of protic solvents such as water or ethanol but is ineffectual at reducing carboxylic acids. The stronger reducing agent lithium aluminium hydride must initially be used in aprotic solvents such as ether as it reacts with water, then the reaction is acidified to obtain the product. Another reducing agent that can be used is hydrogen itself in the presence of a nickel, platinum or palladium catalyst.

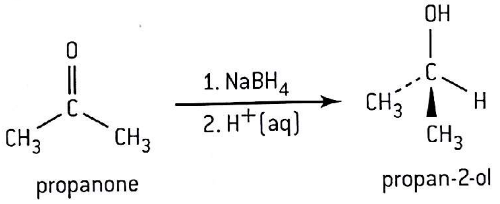
Aldehydes are reduced to primary alcohols.

e.g.



Ketones are reduced to secondary alcohols.

e.g.



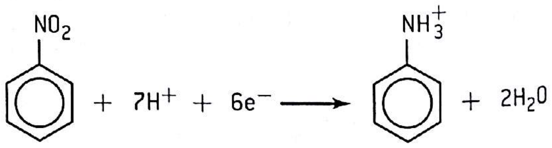
Carboxylic acids are reduced to primary alcohols according to the general equation:

$$RCOOH \xrightarrow[\text{2. } H^+(aq)]{\text{1. } LiAlH_4 \text{ in ether}} RCH_2OH$$

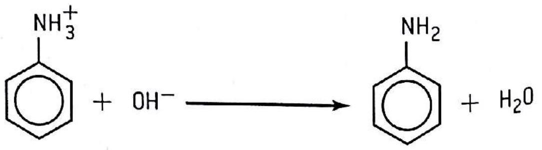
b) Reduction of nitrobenzene

The reduction of nitrobenzene to phenylamine is usually carried out in two stages.

Stage 1. Nitrobenzene is refluxed with a mixture of tin and concentrated hydrochloric acid. The tin provides the electrons by acting as the reducing agent and the product is the phenylammonium ion.



Stage 2. The addition of sodium hydroxide solution releases the free amine.



Synthetic routes

SYNTHESIS AND RETRO-SYNTHESIS

The raw materials for many organic compounds originate from coal, crude oil or natural gas. The challenge for synthetic organic chemists is to devise reaction pathways to make new compounds from simple starting materials using as few steps as possible, each with the highest yield possible. The more steps there are in an organic synthesis, then the lower the final yield is likely to be, because some material will be lost during each step. For example, but-2-ene can be obtained by cracking some of the higher boiling point fractions of crude oil. One way of obtaining butanone from but-2-ene in a two-step process would be, firstly, to hydrate the but-2-ene by heating with steam in the presence of a sulfuric acid catalyst to produce butan-2-ol. This secondary alcohol could then be oxidized with a warm acidified solution of potassium dichromate(VI).

This sub-topic requires organic synthesis using up to four different steps involving reactions that have already been covered. Rather than looking at the specific compounds it is often helpful to look at the functional groups involved and consider the reactions of these groups. For some syntheses it is helpful to work forward from the reactants but it can be equally profitable to work backwards from the product to find the simplest and cheapest starting materials – a process known as retro-synthesis. In the above example butanone is a ketone and ketones are formed by oxidizing secondary alcohols. It can then be seen that alcohols are made by hydrating alkenes. The following is a summary of the reactions covered in the Core and AHL organic chemistry.

- Combustion of hydrocarbons and alcohols
- Substitution of alkanes with halogens
- Addition reactions of alkenes with H_2, H_2O, HX, X_2, interhalogens and polymerization
- Substitution of halogenoalkanes with sodium hydroxide
- Substitution of benzene to form nitrobenzene
- Reduction of nitrobenzene to form phenylamine
- Oxidation of alcohols and aldehydes
- Reduction of aldehydes, ketones and carboxylic acids
- Esterification

When devising syntheses, the reagents and all necessary experimental conditions should be given. Often more than one solution will be possible as the same product may be obtained by different routes. For example, bromoethane can be prepared from ethene either by adding hydrogen bromide directly to ethene or by first converting the ethene into ethane then reacting it with bromine in ultraviolet light.

WORKED EXAMPLES OF SYNTHESES

1. Starting with benzene, suggest a two-step synthesis of phenylamine.

Working backwards, phenylamine can be obtained by reducing nitrobenzene, which can be obtained from benzene by electrophilic substitution.

Step 1. React benzene with a mixture of concentrated nitric acid and concentrated sulfuric acid at 50 °C to form nitrobenzene.

$$C_6H_6 + HNO_3(\text{conc}) \xrightarrow[50\ ^\circ C]{H_2SO_4\ (\text{conc})} C_6H_5NO_2 + H_2O$$

Step 2. Reflux nitrobenzene with tin and concentrated hydrochloric acid, then react with sodium hydroxide solution.

$$C_6H_5NO_2 \xrightarrow[OH^-\ (aq)]{Sn/HCl,\ \text{reflux}} C_6H_5NH_2$$

2. Starting with propane, suggest a four-step synthesis of propyl propanoate.

Propane reacts with halogens to form halogenoalkanes, which can easily be converted into alcohols which are required to make an ester. A primary alcohol can also be oxidized to a carboxylic acid which will also be required to make the ester.

Step 1. React propane with bromine in ultraviolet light to give 1-bromopropane (other halogenated products will need to be discarded).

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{UV} CH_3CH_2CH_2Br + HBr$$

Step 2. React 1-bromopropane with warm dilute aqueous sodium hydroxide solution to give propan-1-ol.

$$CH_3CH_2CH_2Br + NaOH \xrightarrow{\text{warm}} CH_3CH_2CH_2OH + NaBr$$

Step 3. Keep half of the propan-1-ol and reflux the remainder with warm excess acidified potassium dichromate(VI) solution to convert it into propanoic acid.

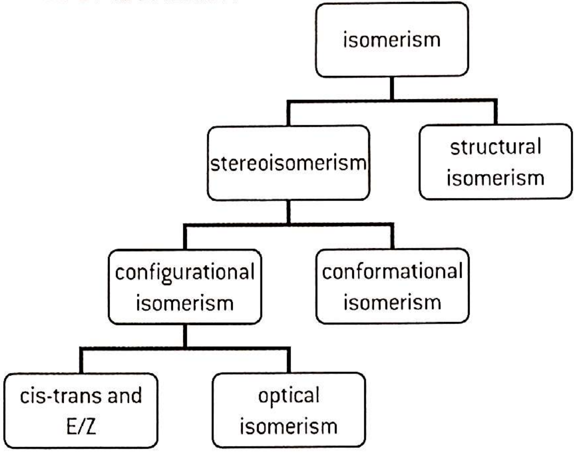
$$CH_3CH_2CH_2OH + \xrightarrow{Cr_2O_7^{2-}/H^+,\ \text{reflux}} CH_3CH_2CHOOH$$

Step 4. Warm propan-1-ol and propanoic acid in the presence of a few drops of concentrated sulfuric acid as a catalyst to make the ester.

$$CH_3CH_2CH_2OH + CH_3CH_2COOH \xrightarrow{H^+} CH_3CH_2COOCH_2CH_2CH_3 + H_2O$$

Stereoisomerism (1)

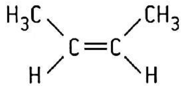
TYPES OF ISOMERISM



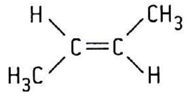
Isomers are compounds that are composed of the same elements in the same proportions but differ in properties because of differences in the arrangement of atoms. Structural isomers share the same molecular formula but have different structural formulas. That is, their atoms are bonded in different ways. Stereoisomers have the same structural formula but differ in their spatial arrangement. Stereoisomers can be sub-divided into two classes – conformational isomers, which interconvert by rotation about a σ bond, and configurational isomers that interconvert only by breaking and reforming a bond. The IB syllabus on stereoisomerism is concerned with configurational isomers which can be further sub-divided into cis–trans and *E*/*Z* isomers (which together used to be known by the now obsolete term of geometrical isomers) and optical isomers.

CIS–TRANS ISOMERISM

Both cis–trans and *E*/*Z* isomerism occur when rotation about a bond is restricted or prevented. The classic examples of cis–trans isomerism occur with asymmetric non-cyclic alkenes of the type $R_1R_2C{=}CR_1R_2$. 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.



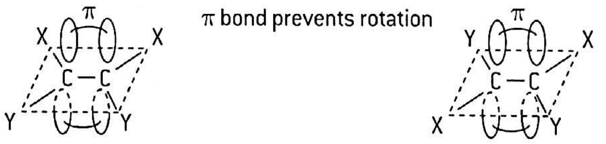
cis-



trans-

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.

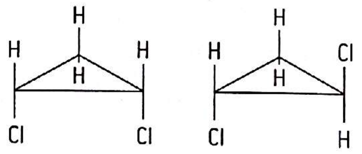
Cis-trans isomerism will always occur in alkenes when the two groups X and Y attached to each of the two carbon atoms are different.



π bond prevents rotation

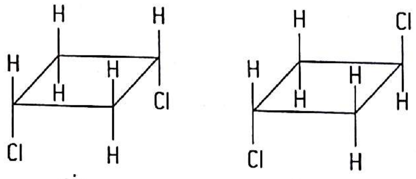
cis- *trans-*

Cis–trans 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.



cis- *trans-*

1,2-dichlorocyclopropane



cis- *trans-*

1,3-dichlorocyclobutane

HL Stereoisomerism (2)

E/Z ISOMERISM

Cis–trans isomerism is a restricted form of *E*/*Z* isomerism as it only occurs when the two substituents R_1 and R_2 (or X and Y) occur on either side of the carbon to carbon double bond. *E*/*Z* isomerism covers every case where free rotation around a C=C double bond is not possible, i.e. for $R_1R_2C{=}CR_3R_4$ where ($R_1 \neq R_2$, $R_3 \neq R_4$) and where neither R_1 nor R_2 need be different from R_3 or R_4.

E/*Z* terminology is quite easy to apply and depends on what are known as the Cahn–Ingold–Prelog (CIP) rules for determining the priority of the atoms or groups attached to the two carbon atoms of the double bond. Each of these two carbon atoms on either side of the double bond is considered separately. In simple terms the higher the atomic number of the attached atoms to each carbon atom the higher the priority. Consider 1,2-dichloroethene. Chlorine has a higher atomic number than hydrogen so has a higher priority. If the two atoms/groups lie on the same side the isomer is *Z* and if they lie on opposite sides they are *E*. In this simple case *Z* is the cis-form and *E* is the trans- form.

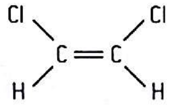
However *Z* does not always equate to cis. If you consider 2-chlorobut-2-ene then the carbon atom of the methyl group has priority over the hydrogen atom on one side of the double bond but because chlorine has a higher atomic number than carbon the chlorine atom has priority over the methyl group on the other side of the double bond. Now the cis-isomer is the E isomer and the trans-isomer is the *Z* isomer.

E/*Z* and not cis–trans must be used when the groups are all different. Consider 2-bromo-1-chloro-2-iodoethene. It is not obvious which would be the cis- and trans- forms. However using the Cahn–Ingold–Prelog rules the *E* and *Z* forms can easily be determined.

Z and *E* both come from German words. *Z* is from *zusammen* (together) and *E* is from *entgegen* (opposite). One easy way to remember the correct application is that *E* could stand for enemy, and enemies are on opposite sides.

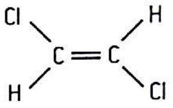
Cl has a higher priority than H on the left-hand side and on the right-hand side.

Both highest priorities lie on the same side so *Z* isomer.



cis-1, 2-dichloroethene
(*Z*)-1, 2-dichloroethene

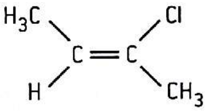
Highest priorities lie on opposite side so *E* isomer.



trans-1, 2-dichloroethene
(*E*)-1, 2-dichloroethene

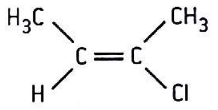
CH_3– has a higher priority than H on the left-hand side and Cl has a higher priority than CH_3– on the right-hand side.

Both highest priorities lie on the same side so *Z* isomer.



trans-2-chlorobut-2-ene
(*Z*)-2-chlorobut-2-ene

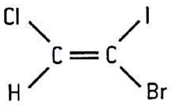
Highest priorities lie on opposite side so *E* isomer.



cis-2-chlorobut-2-ene
(*E*)-2-chlorobut-2-ene

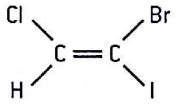
Cl has a higher priority than H on the left-hand side and I has a higher priority than Br on the right-hand side.

Both highest priorities lie on the same side so *Z* isomer.



(*Z*)-2-bromo-1-chloro-2-iodoethene

Highest priorities lie on opposite side so *E* isomer.

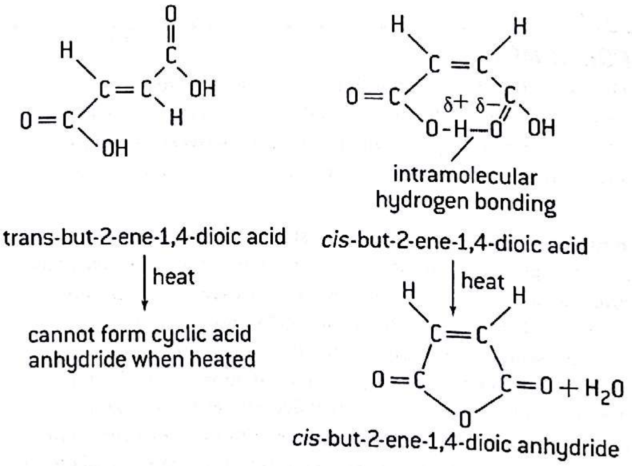


(*E*)-2-bromo-1-chloro-2-iodoethene

PHYSICAL AND CHEMICAL PROPERTIES OF *E/Z* AND CIS–TRANS *ISOMERS*

The chemical properties of E/Z and cis–trans 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.

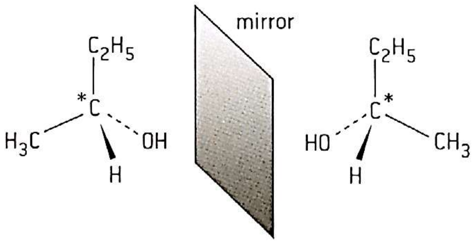
The cis- isomer reacts when heated to lose water and form a cyclic acid anhydride. The trans- isomer cannot undergo this reaction.



HL Stereoisomerism (3)

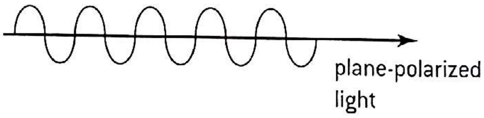
OPTICAL ISOMERISM

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, also known as a stereocentre. The two isomers are known as enantiomers and are mirror images of each other. Examples include butan-2-ol, $CH_3CH(OH)C_2H_5$, 2-hydroxypropanoic acid (lactic acid), $CH_3CH(OH)COOH$ and all amino acids (except glycine, NH_2CH_2COOH).



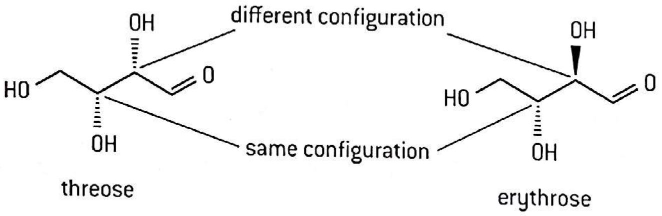
enantiomers of butan-2-ol
(* asymmetric carbon/chiral carbon/stereocentre)

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-polarized 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-polarized 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 $H_2NCH(CH_2CONH_2)COOH$ tastes bitter whereas the other enantiomer tastes sweet.

If a molecule contains two or more stereocentres then several different stereoisomers are possible. They are known as enantiomers if they are mirror images and as diastereomers if they are not mirror images of each other. Diastereomerism occurs when two or more stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent stereocentres. This is particularly important with many sugars and some amino acids. Diastereomers have different physical properties and different chemical reactivity. e.g.

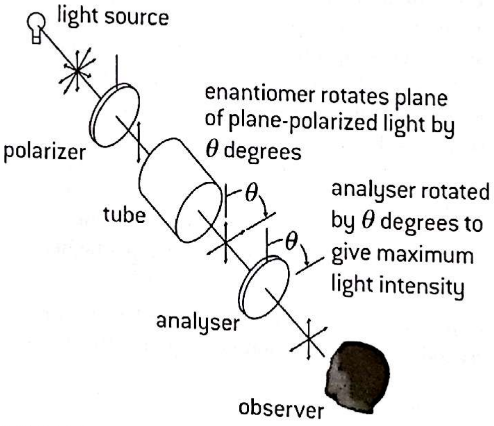


diastereomers of 2, 3, 4-trihydroxybutanal

POLARIMETRY

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 dissolved in a suitable solvent.

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**.



MULTIPLE CHOICE QUESTIONS – ORGANIC CHEMISTRY

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

   A. CH_3COOH and $HCOOCH_3$

   C. C_2H_4 and C_2H_6

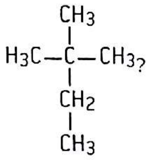
   B. CH_3OH and C_2H_5OH

   D. C_2H_5Cl and $C_2H_4Cl_2$

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

   A. 1　　B. 2

   C. 3　　D. 4

3. Applying IUPAC rules what is the name of  $H_3C-\overset{CH_3}{\underset{\underset{CH_3}{|}}{\underset{CH_2}{\underset{|}{\overset{|}{C}}}}}-CH_3$?

   A. 2-methyl-2-ethylpropane　　C. 2,2-dimethylbutane

   B. hexane　　D. 2-methylpentane

4. 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 $Cl^{\bullet}$ radicals.

   C. It involves homolytic fission and Cl^- ions.

   D. It involves homolytic fission and $Cl^{\bullet}$ radicals.

5. Which compound is an ester?

   A. CH_3COOH　　C. C_2H_5CHO

   B. $CH_3OC_2H_5$　　D. $HCOOCH_3$

6. 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

7. 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. $(CH_3)_3CBr$

8. The reaction between bromine and ethene in the dark is an example of:

   A. free radical substitution

   B. esterification

   C. nucleophilic substitution

   D. addition

9. Which alcohol cannot be oxidized by an acidified solution of potassium dichromate(VI)?

   A. $(CH_3)_3COH$　　C. $(CH_3)_2CHCH_2OH$

   B. $CH_3CH_2CH_2CH_2OH$　　D. $CH_3CHOHCH_2CH_3$

HL

10. 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 and III only　　D. I, II and III

11. The product from the reaction of iodine monochloride, ICl, with pent-1-ene is:

    A. $CH_3CH_2CHICHClCH_3$　　C. $CH_3CH_2CH_2CHClCH_2I$

    B. $CH_3CH_2CH_2CHICH_2Cl$　　D. $CH_3CH_2CHClCHICH_3$

12. Ketones are reduced by sodium borohydride, $NaBH_4$, to give:

    A. a primary alcohol　　C. a tertiary alcohol

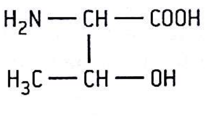
    B. a secondary alcohol　　D. a carboxylic acid

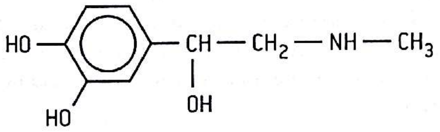
13. During the conversion of nitrobenzene to phenylamine (aniline) by tin and concentrated hydrochloric acid the organic intermediate is:

    A. the phenylammonium ion　　C. phenol

    B. dinitrobenzene　　D. chlorobenzene

14. Which can exist as enantiomers and diastereomers?

    I. 

    II. 

    III. $CH_3CH(OH)CH_2CH(OH)CHO$

    A. I and II only　　C. II and III only

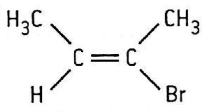
    B. I and III only　　D. I, II and III

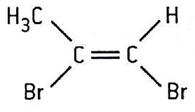
15. How many four-membered ring isomers are there of dichlorocyclobutane, $C_4H_6Cl_2$?

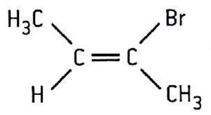
    A. 3　　C. 5

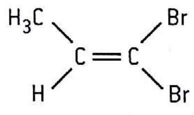
    B. 4　　D. 6

16. Which is an *E* isomer?

    A. 

    C. 

    B. 

    D. 

17. An organic compound is prepared from ethanol by a four-step synthesis. Each step gives a yield of 70%. What will be the yield of the organic compound based on the initial amount of ethanol?

    A. 24%　　C. 34%

    B. 28%　　D. 70%

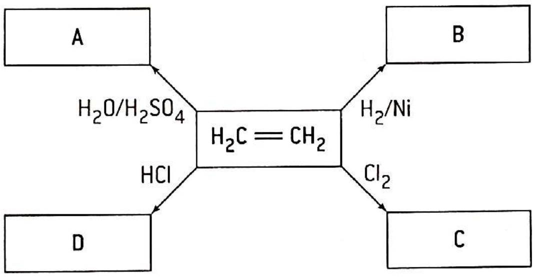
SHORT ANSWER QUESTIONS – ORGANIC CHEMISTRY

1. Alkenes are important starting materials for a variety of products.

   a) State and explain the trend of the boiling points of the first five members of the alkene homologous series. [3]

   b) Describe two features of a homologous series. [2]

   c) Below is a schematic diagram representing some reactions of ethene. The letters **A–D** represent the organic compounds formed from the reactants and catalysts shown.

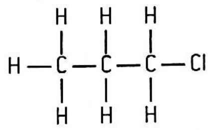


   Deduce the structural formulas of compounds **A**, **B**, **C** and **D** and state the IUPAC name of compound **C**. [5]

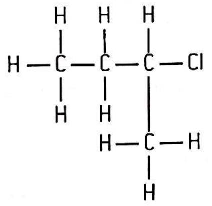
   d) Describe a chemical test that could be used to distinguish between pent-1-ene and pentane. [2]

   e) State and explain whether the following molecules are primary, secondary or tertiary halogenoalkanes. [4]

E:

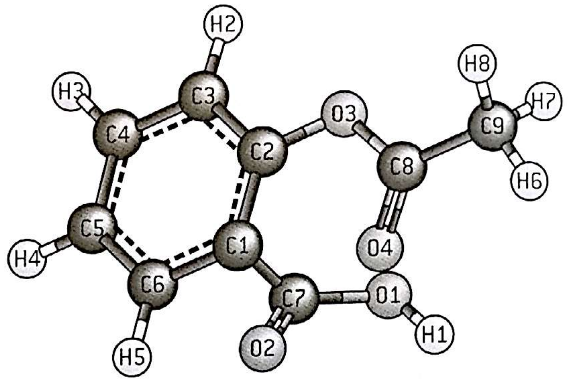


F:



   f) Explain, using equations, the initiation, propagation and termination steps in the free-radical mechanism of the reaction of methane with chlorine. [4]

2. The following is a three-dimensional computer-generated representation of aspirin. Each carbon, oxygen and hydrogen atom has been given a unique number.



   a) Identify **one carbon** atom that is part of

      (i) the phenyl functional group.

      (ii) the carboxylic acid group.

      (iii) the ester group. [3]

   b) Explain why the bond between C_8 and O_3 is longer than the bond between C_8 and O_4. [2]

   c) Compare the length of the bond between C_1 and C_6 with the bond between C_1 and C_7. [2]

   d) Explain how a primary alcohol can be converted into

      (i) a carboxylic acid

      (ii) an ester. [4]

HL

3. Consider alkenes with the molecular formula C_5H_9Br. Give structural formulas for one isomer which shows

   a) no stereoisomerism [1]

   b) optical but no cis–trans or *E/Z* isomerism [1]

   c) optical, trans- and *E* isomerism [1]

   d) optical, cis- and *Z* isomerism. [1]

   e) trans- and *Z* isomerism but no optical isomerism [1]

   f) cis- and *E* isomerism but no optical isomerism. [1]

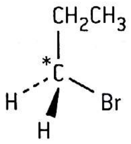
4. State the equations for each step and any necessary inorganic reagents and conditions for:

   a) The preparation of propyl propanoate by a **two**-step synthesis using propan-1-ol as the only organic reagent. [4]

   b) The preparation of propanone by a **three**-step synthesis using propene as the only organic reagent. [6]

   c) The preparation of propanal by a **four**-step synthesis using propene as the only organic reagent. [8]

5. 1-bromopropane undergoes a substitution reaction with warm aqueous sodium hydroxide solution.



   a) Explain why the substitution occurs on the carbon atom that is marked as *C. [1]

   b) State the rate equation for this reaction and identify the name of the reaction mechanism. [2]

   c) Explain the mechanism of the reaction using curly arrows to represent the movement of electron pairs during the substitution. [4]

   d) Explain how changing the halogenoalkane to 1-chloropropane would affect the rate of the substitution reaction. [2]

6. Benzene can be nitrated to form nitrobenzene by warming with a mixture of concentrated nitric acid and concentrated sulfuric acid. Explain, with any necessary equations, the role of the concentrated sulfuric acid in this reaction. [6]