

10.1 Fundamentals of organic chemistry

Homologous series

Organic compounds are classified into families known as **homologous series**. Members of each series possess similar properties:

- Successive members of a homologous series differ by a CH_2 group
- Members of homologous series can be represented by the same general formula
- Members of homologous series contain the same functional group
- There is a trend in the physical properties
- There is a similarity in the chemical properties

Empirical, molecular and structural formulae

Empirical formulae show the simplest whole number ratio of the atoms in a molecule

Molecular formulae show the actual number of atoms of each element present in a molecule

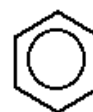
Structural formulae are representations of molecules showing how the atoms are bonded to each other:

- A **full structural formula** shows every bond and atom
- A **condensed structural formula** omits bonds where they can be assumed, and groups atoms
- A **stereochemical formula** attempts to show the relative positions of atoms in 3D

The table below shows examples of these formulae in use:

Compound	Ethane	Ethanoic acid	Glucose
Empirical formula	CH_3	CH_2O	CH_2O
Molecular formula	C_2H_6	$\text{C}_2\text{H}_4\text{O}_2$	$\text{C}_6\text{H}_{12}\text{O}_6$
Full structural formula			
Condensed structural formula	CH_3CH_3	CH_3COOH	$\text{CHO}(\text{HCOH})_4\text{CH}_2\text{OH}$

In some cases we do not need to show the exact details of the hydrocarbon, or alkyl, part of the molecule, so we can abbreviate this to **R**. For molecules with a benzene ring, C_6H_6 , we use the following symbol to show the ring:




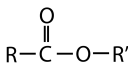

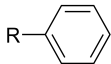


IUPAC system for nomenclature of organic compounds

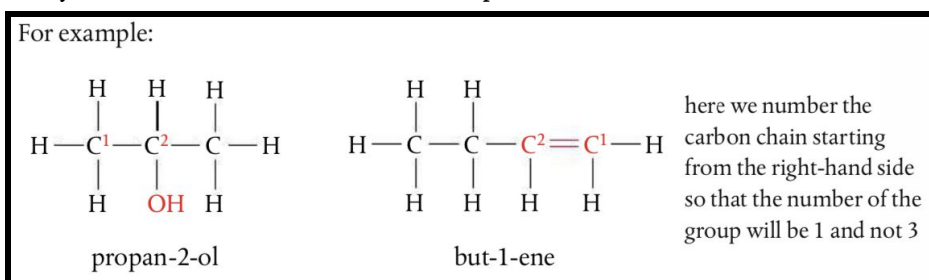
Rule 1: Identify the longest straight chain of carbon atoms

Number of carbon atoms in the longest chain	1	2	3	4	5	6
Stem in IUPAC name	Meth-	Eth-	Prop-	But-	Pent-	Hex-

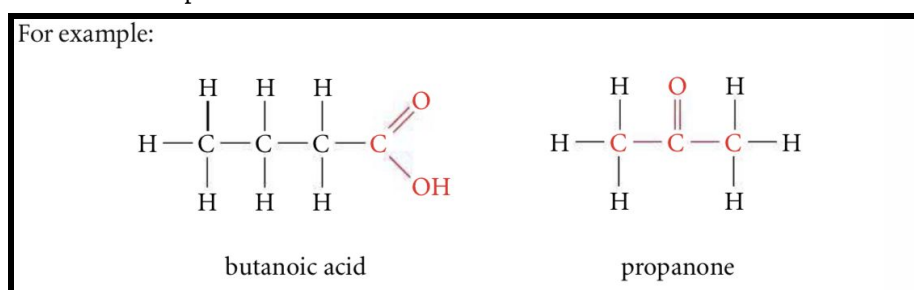
Rule 2: Identify the functional group

Class	Functional group	Name of group	Suffix in IUPAC name	General formula	Example compound
Alkane		Alkanyl	-ane	C_nH_{2n+2}	C_2H_6 , Ethane
Alkene	$C=C$	Alkenyl	-ene	C_nH_{2n}	$H_2C=CH_2$, Ethene
Alkyne	$C\equiv C$	Alkynyl	-yne	C_nH_{2n-2}	$HC\equiv CH$, Ethyne
Alcohol	$-OH$	Hydroxyl	-anol	$C_nH_{2n+1}OH$	C_2H_5OH , Ethanol
Ether	$R-O-R'$	Ether	-oxyalkane	$R-O-R'$	$H_3C-O-C_2H_5$ Methoxyethane
Aldehyde		Aldehyde	-anal	$R-CHO$	C_2H_5CHO Propanal
Ketone		Carbonyl	-anone	$R-CO-R'$	CH_3COCH_3 Propanone
Carboxylic acid		Carboxyl	-anoic acid	$C_nH_{2n+1}COOH$	C_2H_5COOH Propanoic acid
Ester		Ester	-yl, -anoate	$R-COO-R'$	$C_2H_5COOCH_3$ Methyl propanoate
Carboxy Amide		Carboxamide	-anamide		$C_2H_5CONH_2$ Propanamide
Amine	$-NH_2$	Amine	-anamine		$C_2H_5NH_2$ Ethanamine
Nitrile	$-C\equiv N$	Nitrile	-anenitrile		C_2H_5CN Propanenitrile
Arene		Phenyl	-benzene		$C_6H_5CH_3$ Methyl benzene

The position of the functional group in the molecule is shown by a number between dashes inserted before the functional group ending. The number refers to the carbon atom to which the functional group is attached. We try to make this the smallest number possible:



In some cases, it is only possible for the functional group to be one place, so in these cases we don't need to give a number to show its position:



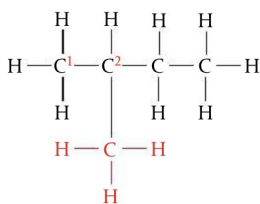
Rule 3: Identify the side chains or substituent groups

Side chains, or functional groups in addition to the one used as the suffix are known as **substituents** and given as the first part of the **prefix**.

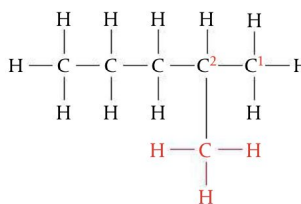
Class	Functional group	Name of functional group	Prefix in IUPAC name	Example
Alkane			Methyl, ethyl, propyl, etc.	$\text{CH}_3\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$ 2-methylbutane $\text{CH}(\text{C}_3\text{H}_7)_3$ 4-propylheptane
Halogenoalkane	-F, -Cl, -Br, -I	Halogeno	Fluoro, chloro, bromo, iodo	$\text{C}_2\text{H}_5\text{Cl}$ Chloroethane $\text{CH}_3\text{CH}_2\text{BrCH}_3$ 2-bromopropane
Amine	-NH ₂	Amine	Amino	$\text{CH}_2(\text{NH}_2)\text{COOH}$ 2-aminoethanoic acid

The position of the substituent groups is given by a number followed by a dash in front of its name showing the carbon atom to which it is attached, again numbering the chain to give the smallest number to the group.

For example:



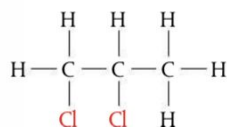
2-methylbutane



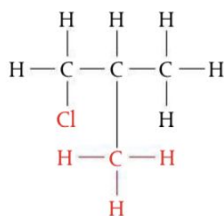
2-methylpentane

If there is more than one substituent group of the same type, we use commas between the numbers and the prefixes di-, tri-, or tetra- before the name. Substituents are given in order of the number of the carbon atom to which they are attached; if there is more than one group on the same atom they are put in alphabetical order.

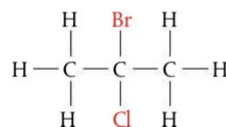
For example:



1,2-dichloropropane



1-chloro-2-methylpropane



2-bromo-2-chloropropane

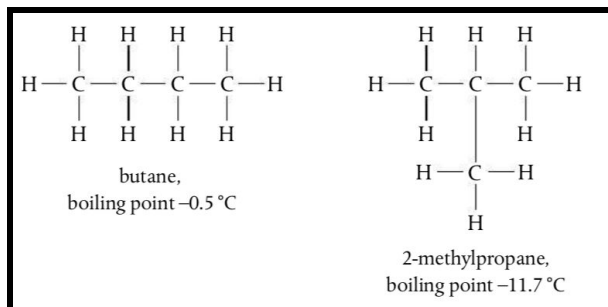
In summary, IUPAC nomenclature has three possible parts, which are written together as a single word:

Prefix	Stem	Suffix
position, number and name of substituents		number of carbon atoms in longest chain		class of compound determined by functional group

Isomers

Structural isomers are molecules that have the same molecular formula but different structures.

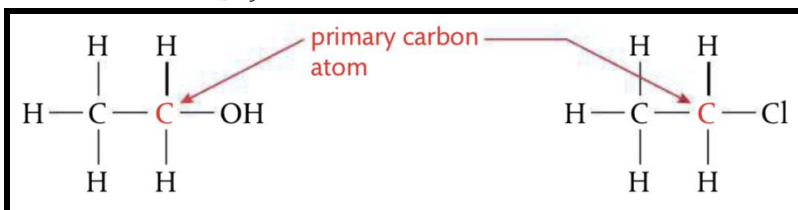
The number of isomers that exist for a molecular formula increases as the molecular size increases. The isomer with the longest straight chain has the highest boiling point, as a longer chain means a longer surface area, so there is more interaction between molecules, so a stronger force of attraction. As such, more energy is required to break this force of attraction.



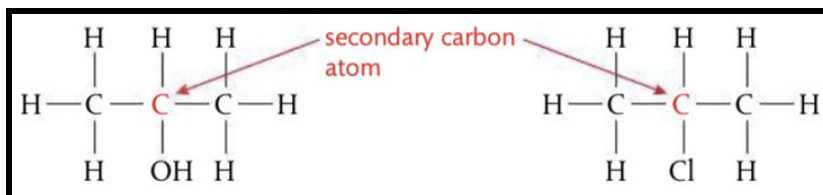
Primary, secondary and tertiary compounds

The activity of a functional group is often influenced by its position in the carbon chain.

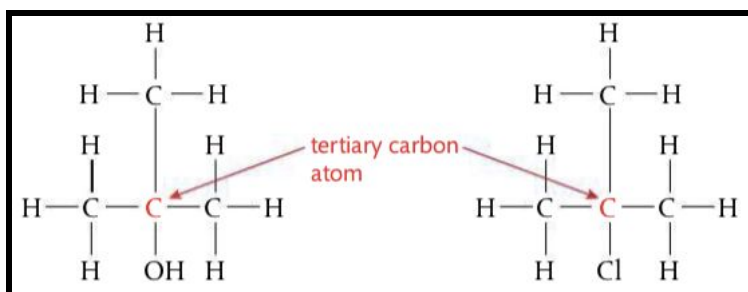
A **primary carbon atom** is attached to the functional group and also to at least two hydrogen atoms. Molecules with this arrangement are known as primary molecules. For example, ethanol, C_2H_5OH is a primary alcohol and chloroethane, C_2H_5Cl , primary halogenoalkane:



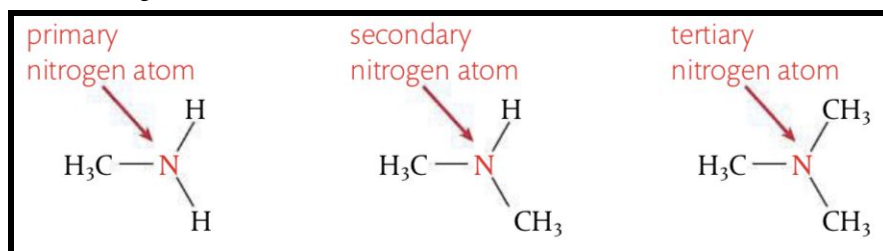
A **secondary carbon atom** is attached to the functional group and also to one hydrogen atom and two alkyl groups. These molecules are known as secondary molecules. For example, propan-2-ol, $CH_3CH(OH)CH_3$, is a secondary alcohol, and 2-chloroethane, $CH_3CHClCH_3$, is a secondary halogenoalkane:



A **tertiary carbon atom** is attached to the functional group and is also bonded to three alkyl groups, and so has no hydrogen atoms. These molecules are known as tertiary molecules. For example, 2-methylpropan-2-ol, $C(CH_3)_3OH$, is a tertiary alcohol, and 2-chloro-2-methylpropane, $C(CH_3)_3Cl$, is a tertiary halogenoalkane:

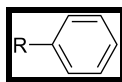


Similar classification can be applied to **amines** according to the number of alkyl groups and hydrogen atoms bonded to the nitrogen atom.



Arenes

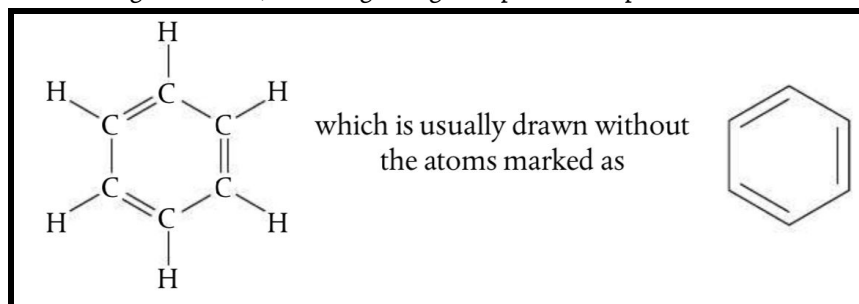
Arenes are a class of compounds that are derived from **benzene**, C_6H_6 . They form a branch of organic compounds known as **aromatics**. Arenes contain a **phenyl functional group**.



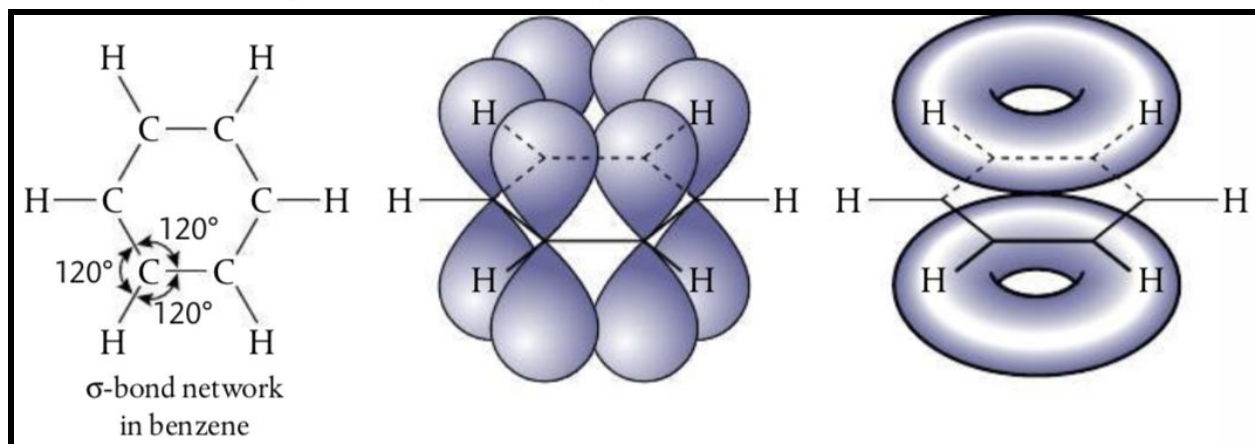
Benzene

Benzene does not behave like other unsaturated molecules. Given its 1:1 ratio of carbon to hydrogen, the molecule is considered highly unsaturated. However, benzene has no isomers, and is reluctant to undergo addition reactions, both features that would be expected from these molecules.

The special stability of the benzene ring is the result of delocalised electrons. Benzene's cyclic structure consists of a framework of six carbon atoms with single bonds between them. Each C atom is sp^2 hybridized, and forms 3 sigma bonds, forming a trigonal planar shape.



This leaves one unhybridized p electron on each C atom, with its dumbbell shape perpendicular to the shape of the ring. Instead of pairing up to form discrete alternating π bonds, the p orbitals effectively overlap in both directions, spreading themselves out evenly to be shared by all six C atoms. This forms a delocalised p electron cloud in which electron density is concentrated in two donut-shaped rings. This lowers the internal energy of the molecule, making it stable.



This model provides evidence for the properties of Benzene discussed below:

Property	Observation/Evidence	Explanation
Bond Lengths	All C-C bonds are equal in length between single and double bonds	Each bond contains a share of 3 electrons between the bonded atoms, so there is a "1.5" bond C-C = 0.154nm C=C = 0.134nm Benzene = 0.139nm
Enthalpy of hydrogenation	Theoretical value based on adding H ₂ across the three double bonds should be -362kJ mol ⁻¹ However, experimental value is -210kJ mol ⁻¹	Delocalisation minimizes electron repulsion, giving benzene a more stable structure, lowering its internal energy by 152kJ mol ⁻¹ . This is the amount of energy required to overcome the special stability of the ring, known as the resonance energy
Type of reactivity	Benzene is reluctant to undergo addition reactions, and is more likely to undergo substitution reactions	Addition reactions aren't favored, as the cloud of electrons would have to be disrupted. The resonance energy would have to be supplied, and the product would be less stable without the cloud. Benzene undergoes substitution reactions, which preserves the stable ring.
Isomers	Only one isomer 1,2-dibromobenzene	As benzene is a symmetrical molecule with no alternating single and double bonds, all adjacent positions in the ring are equal

Trends in physical properties

The hydrocarbon skeleton and the functional group of the compound influence trends in physical properties. The increase in BP with the length of the carbon chain applies to other homologous series too. Branching of the chain also has an effect on volatility, as it influences the strength of intermolecular forces. Branched isomers have less contact with each other than straight chain isomers, and so have weak IM forces and so lower boiling points.

Functional groups also have a significant effect on volatility:

most volatile	least volatile
alkane > halogenoalkane > aldehyde > ketone > alcohol > carboxylic acid	
London (dispersion) force → dipole-dipole interaction → hydrogen bonding	
increasing strength of intermolecular attraction →	
increasing boiling point →	

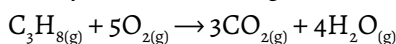
10.2 Functional group chemistry

ALKANES

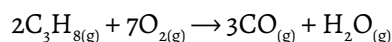
- General formula: C_nH_{2n+2}
- Saturated hydrocarbons

Combustion of alkanes

Alkanes burn in the excess of oxygen to produce carbon dioxide and water. This is known as **complete combustion** because the products are fully oxidised. For eg:

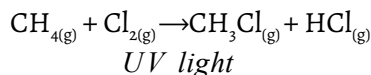


However, when the oxygen supply is limited, incomplete combustion occurs giving rise to carbon monoxide and water. For eg:



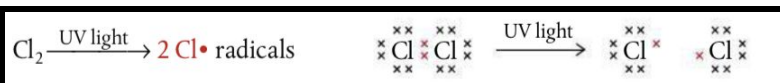
Halogenation of alkanes (free radical substitution)

As alkanes are saturated molecules, the main type of reaction that they can undergo is **substitution**. This occurs when another reactant, such as a halogen, takes the place of a hydrogen atom in the alkane. For example, methane, CH_4 reacts with chlorine producing chloromethane and hydrogen chloride:

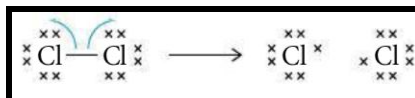


UV light is necessary to break the covalent bond in the chlorine molecule. The UV light splits the chlorine molecule in chlorine atoms, which each have an unpaired electron and are known as **free radicals**. These radicals start a chain reaction in which a mixture of products including the halogenoalkane is formed. This reaction can be described as a sequence of steps known as the **reaction mechanism**:

1) Initiation step

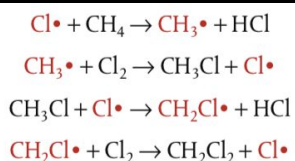


This process occurs in the presence of UV light. It is known as **photochemical homolytic fission**. For simplicity, the initiation step can be shown using curly arrows:



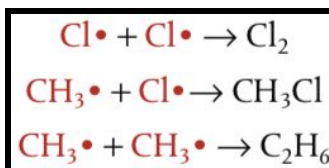
2) Propagation step

There are many possible propagation steps, which all allow the reaction to continue. For this reason, this type of reaction is called a chain reaction



3) Termination step

Termination steps remove free radicals from the mixture by causing them to react together and pair up their electrons



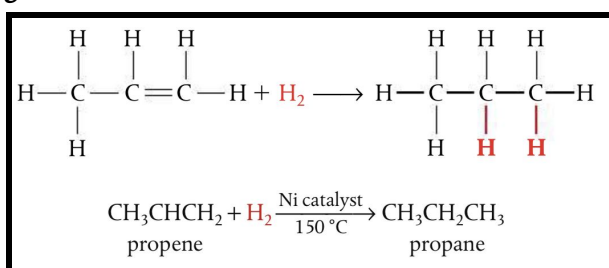
ALKENES

- General formula: C_nH_{2n}
- Alkenes are unsaturated hydrocarbons containing a carbon-carbon double bond

The double bond is made of two different bonds: one σ and π . The carbon atoms are sp^2 hybridized, forming a trigonal planar shape. Alkenes are more reactive than alkanes as the π bond is relatively easily broken, which creates 2 new bonding positions on the C atoms. This enables alkenes to undergo **addition reactions** and so form a range of saturated products.

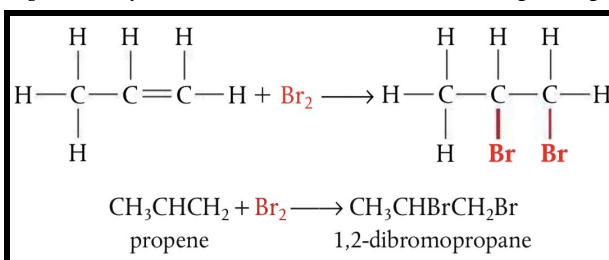
Addition of hydrogen

Alkenes react with hydrogen to form alkanes in the presence of a nickel catalyst at about 150°C . This process is known as **hydrogenation**.



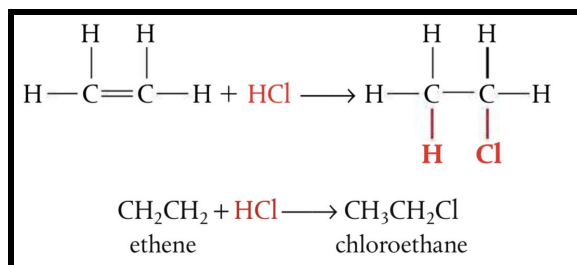
Addition of halogens

Alkenes react with halogens to produce dihalogeno compound. These reactions occur quickly at room temperature, and are accompanied by the loss of colour of the reacting halogen.



Addition of halogen halides

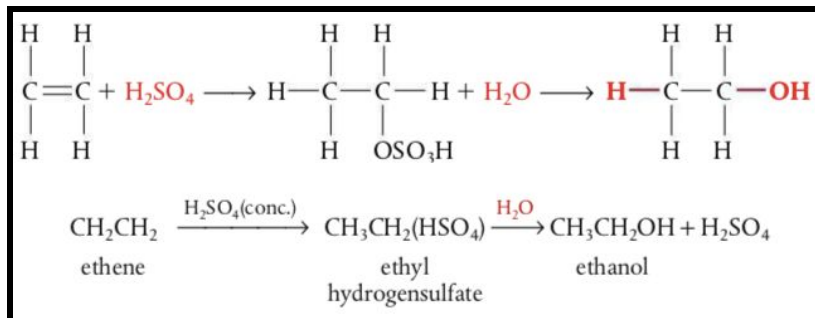
Hydrogen halides such as HCl and HBr react with alkenes to produce halogenoalkanes. These reactions take place rapidly in solutions at room temperature.



Reactivity is in the order $\text{HI} > \text{HBr} > \text{HCl}$ owing to the decrease in the strength of the hydrogen halide bond down group 17. HI, as such, reacts most readily.

Addition of water

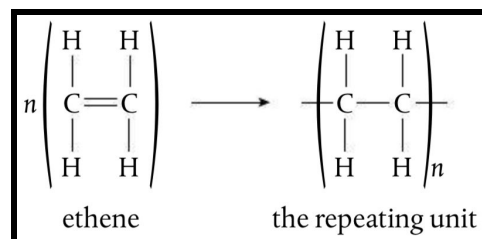
This reaction between alkenes and water is known as **hydration**, and converts the alkene into an alcohol. It can be achieved using H_2SO_4 as a catalyst. The reaction involves an intermediate in which both H^+ and HSO_4^- ions are added across the double bond, but this is quickly followed by hydrolysis with replacement of the HSO_4^- by OH^- and reformation of the H_2SO_4 .



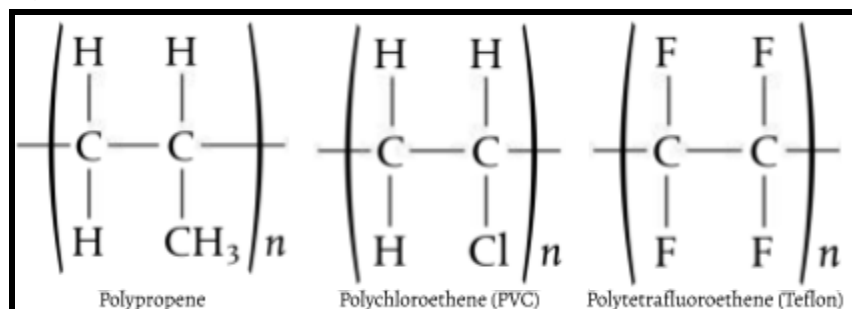
Polymerisation of alkenes

Alkenes readily undergo addition reactions by breaking their double bond, and can be joined together to produce long chains known as **addition polymers**. The alkene used is known as the **monomer**, and its chemical nature determines the properties of the polymer.

Polymers are large molecules, so their structures are shown using a **repeating unit**, which has open bonds at each end. It is put in brackets with n as subscript to denote the number of repeating units. For eg: ethene polymerizes to form polyethene:



Other addition polymers include:



ALCOHOLS

- General formula: $C_nH_{2n+1}OH$
- Alcohols have an $-OH$ functional group

Combustion of alcohols

Like the combustion of hydrocarbons, the complete combustion of alcohols produced carbon dioxide and water. The amount of energy released per mole of alcohol increases as we go up the homologous series as more CO_2 molecules are produced. Comparing methanol and pentanol for eg:



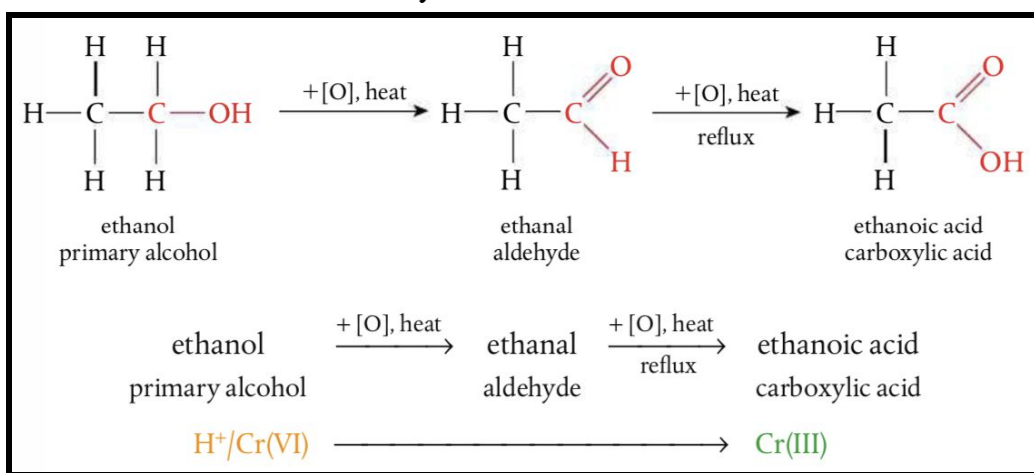
Incomplete combustion of alcohols results in the production of carbon monoxide, just like hydrocarbons

Oxidation of alcohols

Combustion involves the complete oxidation of alcohol molecules, but it is possible for them to react with oxidizing agents which selectively oxidize the carbon atom attached to the $-OH$ group, keeping the carbon skeleton of the molecule intact. This is determined by whether the alcohol is primary, secondary or tertiary.

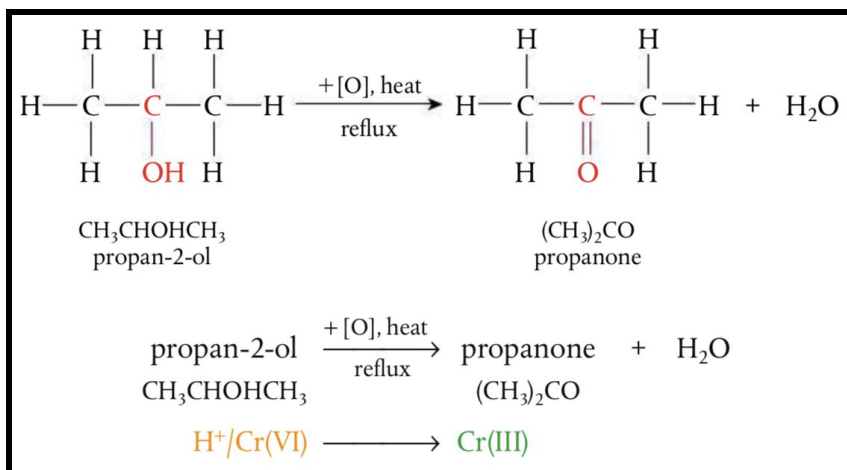
The commonly used oxidizing agent in the lab is **acidified potassium dichromate (VI)**. This is a bright orange solution (because of $Cr(VI)$), which is reduced to green $Cr(III)$ as the alcohol is oxidised on heating. The oxidising agent can be shown as '+[O]'. The oxidation reactions of different alcohols are as follows:

Primary alcohols undergo a 2-step reaction, first forming the **aldehyde**, which under prolonged conditions is oxidized further to the **carboxylic acid**:

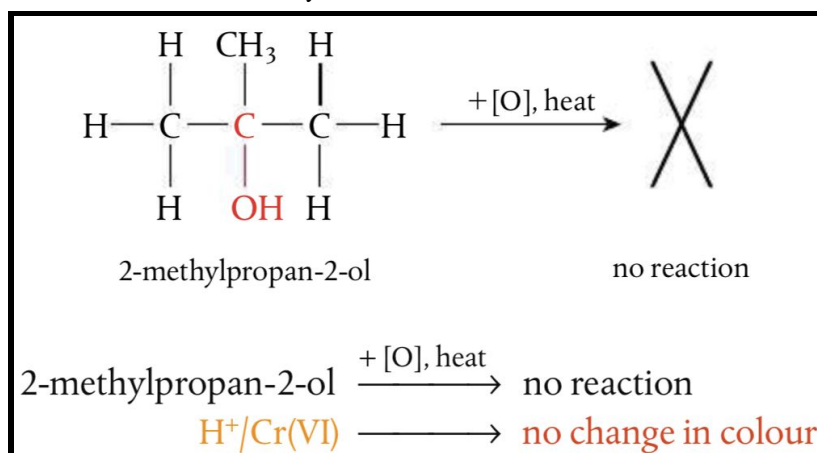


It is possible to stop the reaction after the first step and obtain the aldehyde by **distillation**. Obtaining the carboxylic acid involves leaving the aldehyde in contact with the oxidizing agent for a prolonged period of time - this is achieved using apparatus for a **reflux**.

Secondary alcohols are oxidized to the ketone by a similar process of oxidation:



Tertiary alcohols are not oxidised under comparable conditions. This involves breaking the carbon skeleton of the molecule, which requires a lot more energy. There is no change in the colour of the oxidising agent when reacted with a tertiary alcohol:



A summary of the oxidation of alcohols

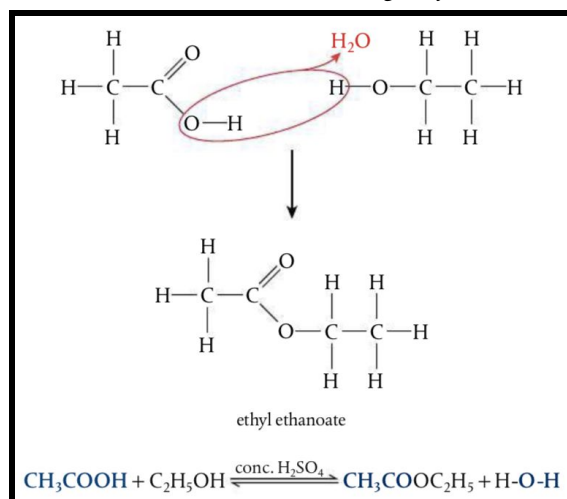
	Oxidation product	Colour change with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (aq)
Primary alcohol	Aldehyde \rightarrow Carboxylic acid	Orange \rightarrow Green
Secondary alcohol	Ketone	Orange \rightarrow Green
Tertiary alcohol	Not oxidised	No colour change

Esters

Alcohols react with carboxylic acids to form esters in a **condensation** reaction in which water is also produced:



For example, ethanoic acid and ethanol react in the following way:



This reaction is an equilibrium reaction, and is catalysed by **concentrated sulfuric acid, H_2SO_4** . The ester has the lowest boiling point of the components of the reaction mixture and so can be separated by distillation. Esters also have distinct smells that are detected when poured into a beaker of water. Esters don't have free —OH groups like their parent acid and alcohol, so cannot form hydrogen bonds. As such, they are insoluble, and tend to form a layer on the surface.

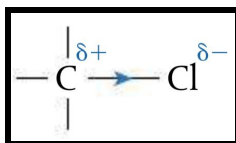
More on Halogenoalkanes and benzene

HALOGENOALKANES

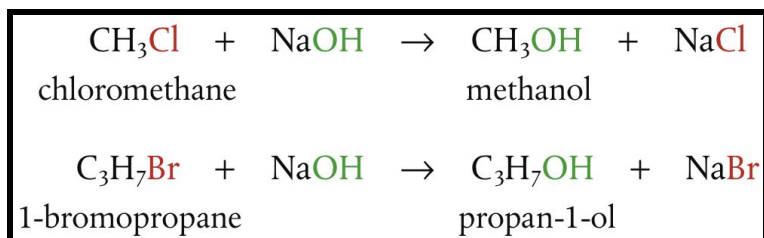
- General formula: $\text{C}_n\text{H}_{2n+1}\text{X}$ {X is the halogen}
- Halogenoalkanes contain an atom of fluorine, chlorine, bromine or iodine bonded to the carbon skeleton of the molecule

Nucleophilic substitution reactions of halogenoalkanes

A **nucleophile** is an electron rich species that is attracted to parts of molecules that are electron deficient. The **polarity in halogeno alkanes is due to the fact the the halogen is more electronegative than carbon, and so exerts a stronger pull on the shared electrons in the carbon-halogen bond**. As such, the halogen gains a partial negative charge, and the carbon gains a partial positive charge (**electron deficient**).



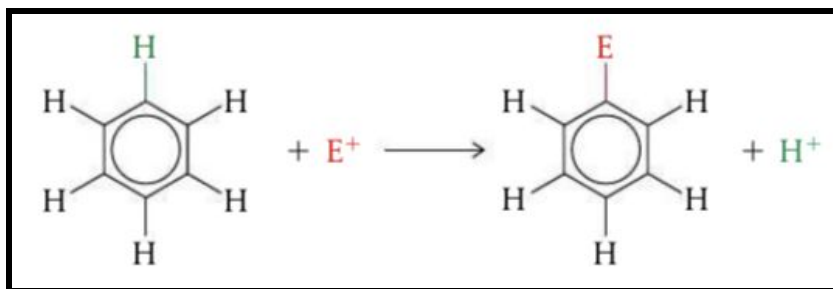
In a halogenoalkane, nucleophiles are attracted to the electron-deficient carbon atom. This leads to reactions in which substitution of the halogen occurs, known as **nucleophilic substitution reactions**. The hydroxide ion is a good nucleophile:



The mechanism and uses of halogenoalkane reactions is discussed further in the HL sections.

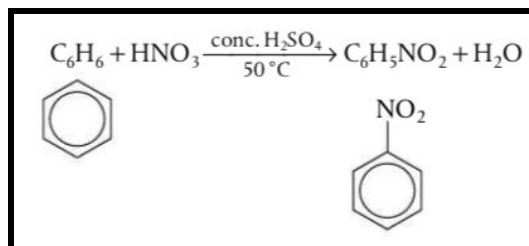
Benzene

Delocalised electrons in benzene give it a special stability. This means that addition reactions, which would lead to the loss of the stable arene ring, are generally not favored as the products would be of higher energy than the reactants. Instead, substitution reactions occur more commonly, as the arene ring is preserved.

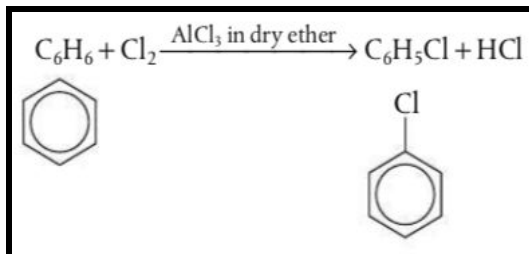


Electrophilic substitution reactions of Benzene

Electrophiles are reactants that are themselves electron deficient as they have a positive charge of a partial positive charge. These species are therefore attracted to the electron rich benzene ring, leading to electrophilic substitution reactions. For eg, benzene reacts with the nitronium ion, NO_2^+ as follows:



Similarly, benzene reacts with halogens:

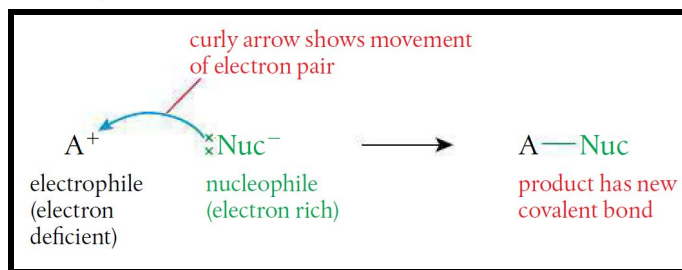


20.1 Types of organic reactions

Nucleophiles are electron rich and attack areas of electron deficiency. They act as Lewis bases and donate a pair of electrons in forming a new covalent bond. Typical examples include OH^- , H_2O , NH_3 , and CN^- .

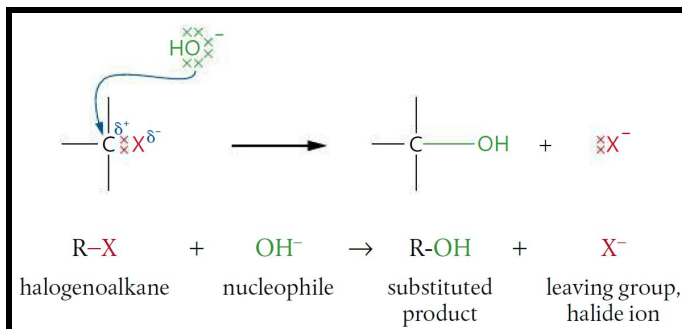
Electrophiles are electron deficient and accept electron pairs from a nucleophile. They act as Lewis acids. Typical examples include H^+ , Br^+ , and NO_2^+ .

A convention used in mechanisms to show the transfer of electrons is the **curly arrow**. The double headed arrow has a tail showing where the electron comes from, and the head showing where it is going:



Nucleophilic substitution reactions: halogenoalkanes

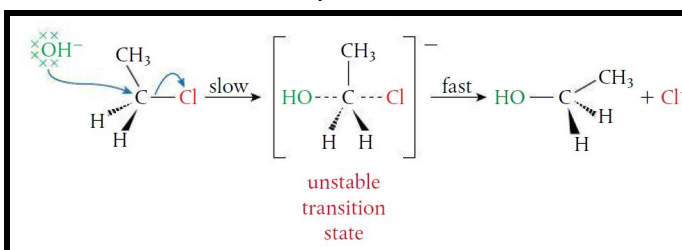
The shorthand notation S_N - substitution nucleophilic - is used for such reactions. The polarity of the carbon halogen bond in halogenoalkanes means that the C atom is electron deficient, and it is attacked by nucleophiles such as OH^- . In these reactions, the carbon halogen bond breaks, and the halogen is released as a negative ion. This type of bond breakage, where both shared electrons go to one product, is known as **heterolytic fission**. The halogen, because it becomes detached, is known as the **leaving group**.



The exact mechanism followed by the reaction depends on whether the halogenoalkane is primary, secondary or tertiary.

Primary halogenoalkanes: S_N2 mechanism

Primary halogenoalkanes have at least 2 H atoms attached to the carbon of the carbon halogen bond. For example when chloroethane reacts with sodium hydroxide:



H atoms are very small, so the C atom is relatively open to attack by the nucleophile. An unstable transition state is formed where the C is weakly bonded to both the halogen and the nucleophile. The carbon halogen bond subsequently breaks heterolytically to form the alcohol and Cl^- .

This is a one-step reaction with an unstable transition state. Because the mechanism is dependent on the concentration of both the halogenoalkane and the OH^- , it is a **bimolecular reaction**:

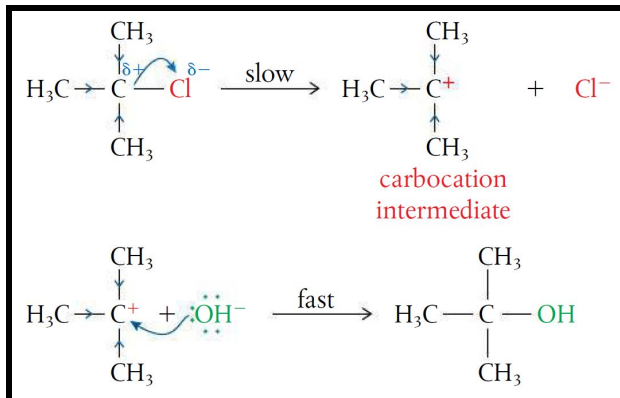
$$\text{Rate} = k[\text{halogenoalkane}][\text{nucleophile}]$$

This explains the naming of the mechanism as S_N2 : substitution nucleophilic bimolecular. Furthermore, the nucleophile attacks the electrophilic carbon atom on the opposite side of the leaving group, which causes an **inversion** of the arrangement of the atoms around the carbon atom.

The S_N2 mechanism is described as **stereospecific** because the three dimensional arrangement of the reactants determines the three dimensional arrangement of the products. The mechanism is favored by polar, aprotic solvents. These are solvents that are not able to form hydrogen bonds, although they may have strong dipoles. This means that they solvate the metal cation rather than the nucleophile. The unsolvated, bare nucleophile has a higher energy state, increasing the reaction rate. Suitable solvents include propanone and ethanenitrile.

Tertiary halogenoalkanes: S_N1 mechanism

Tertiary halogenoalkanes have at least 3 alkyl groups attached to the carbon of the carbon halogen bond. For example the reaction of 2-chloro-2-methylpropane with NaOH:



The presence of three alkyl groups around the carbon of the carbon halogen causes **steric hindrance**, meaning that these bulky groups make it difficult for an incoming group to attack this carbon atom.

Instead step 1 involves the halogenoalkane ionizing by breaking its carbon halogen bond heterolytically. As the halide ion is detached, the C atom has a temporarily positive charge known as a **carbocation intermediate**. The nucleophile attacks this in the second step of the reaction, leading to the new bond.

Another reason why this mechanism is favored is the fact that the three alkyl groups are able to stabilize the carbocation, as each of these has a **positive inductive effect**. This ensures that the carbocation is stable for long enough for the second step to occur.

Step 1 is the slow step, and includes only the halogenoalkane, so this is a **unimolecular reaction**:

$$\text{Rate} = k[\text{halogenoalkane}]$$

This explains the naming of the mechanism as S_N1 : substitution nucleophilic unimolecular. The planar shape of the carbocation allows the nucleophile to attack from any position in step 2. This leads to the formation of optical isomers in a racemic mixture.

The influence of solvents on the reaction is a result of their ability to stabilize the carbocation. Anything that stabilizes the intermediate will favour the reaction. Polar, protic solvents are able to form hydrogen bonds and so are effective in stabilizing the positively charged intermediate by solvation involving ion-dipole interactions. Suitable solvents include water, alcohols and carboxylic acids.

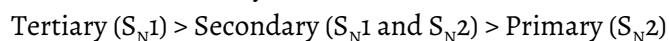
Secondary halogenoalkanes

It is not possible to be precise about the mechanism of nucleophilic substitution in secondary halogenoalkanes, as data show that they usually undergo a mixture of both S_N1 and S_N2 mechanisms.

Factors affecting the rate of nucleophilic substitution:

- **The effect of the mechanism**

Experiments show that the S_N1 mechanism proceeds more quickly than the S_N2 mechanism. So reactions occur more quickly with tertiary halogenoalkanes than with primary halogenoalkanes. Secondary halogenoalkanes using a mixture of both mechanisms show an intermediate rate of reaction. The relative rate of reactivity of the three classes with other variables constant is;



- **The influence of the halogenoalkane (leaving group)**

- There are two factors to consider:

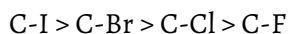
- Polarity of the carbon halogen bond

As electronegativity of halogens decreases down group 17, the C on the carbon halogen bond becomes less electron deficient and so less vulnerable to nucleophilic attack. So we would expect:

fluoroalkane > chloroalkane > bromoalkane > iodoalkane

- Strength of the carbon halogen bond

Bond energy data shows that this bond decreases in strength going down G17. As the substitution involves breaking this bond, we would expect the ease of breaking bonds to be:



Reaction rate data shows that it is the bond strength that determines the outcome here. The relative rate of reaction of the different halogenoalkanes when all other variables are kept constant is therefore:

Iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes

- **Choice of solvent**

- S_N1 is favored by protic solvents whereas S_N2 is favored by aprotic solvents

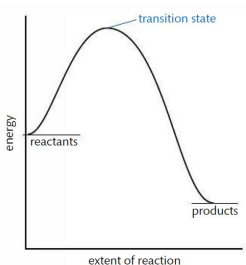
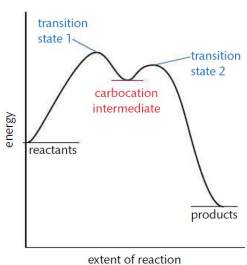
- Polar, aprotic solvents have no hydrogen bonding so S_N2 reactions are favored since nucleophiles do not solvate effectively so have an enhanced effect on nucleophilicity of anionic nucleophiles

- Polar protic solvents favour S_N1 reactions since the carbocation intermediate is solvated by ion-dipole interactions by the polar solvent

- So the fastest reaction occurs in tertiary iodoalkanes in protic solvents

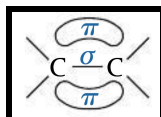
- S_N1 reactions can be followed by the appearance of the halide ion. AgNO_3 , added to the mixture reacts with the halide ion to form a precipitate of silver halide:

The table below summarizes the differences in the two types of nucleophilic substitution:

	S_N2	S_N1
Favoured by	Primary halogenoalkanes	Tertiary halogenoalkanes
Nature of mechanism	Concerted one-step reaction with unstable transition state	Two-step reaction via carbocation intermediate
Relative rate	Lower	Higher
Favoured solvent	Polar, aprotic	Polar, protic
Reaction profile		

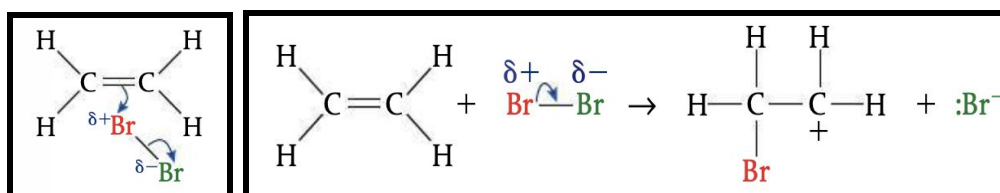
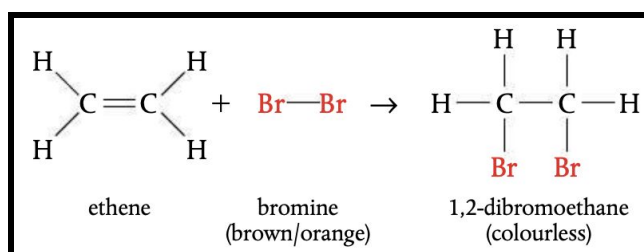
Electrophilic addition reactions: alkenes

Alkenes are unsaturated molecules, allowing them to undergo addition reactions. To understand why this is the case, we can look at the features of the C=C bond:



C atoms of the double bond are sp^2 hybridized, forming a planar triangular shape, a fairly open structure that makes it relatively easy for incoming groups to attack. Because the electrons in the pi bond are less closely associated with the nuclei, it is a weaker bond than the sigma bond and so breaks more easily during addition reactions. Being an area of electron density, the pi bond is attractive to nucleophiles. Below are some example reactions:

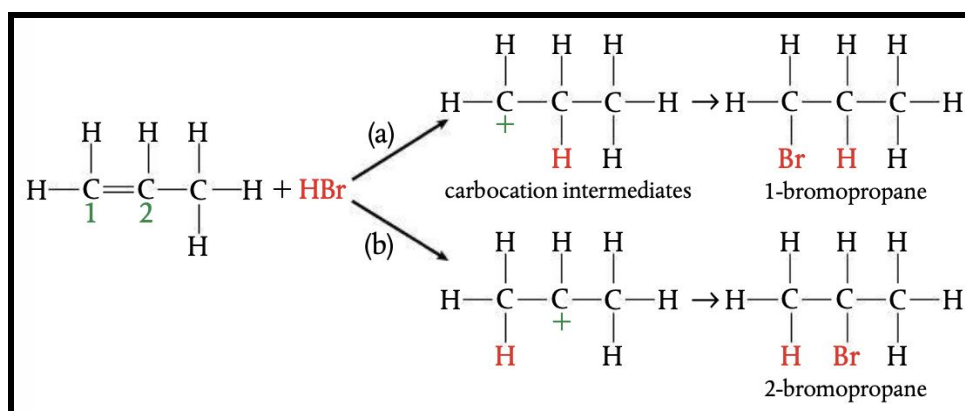
- Ethene + bromine



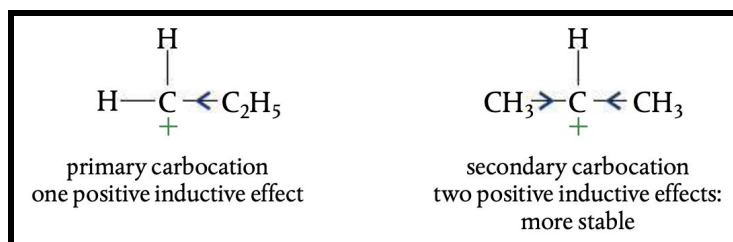
A Br_2 molecule is polarized when it approaches the electron rich region of the alkene. The bromine splits heterolytically, and the Br^+ attacks ethene. The next steps are slow, involving the formation of a positively charged carbocation. This unstable species then reacts with Br^- ion to form 1,2-dibromoethane.

- Ethene + hydrogen bromide, propene + bromine all follow similar mechanisms
- Propene + hydrogen bromide (asymmetric addition)

When an unsymmetrical alkene such as propene is reacted with a hydrogen halide such as HBr , there are theoretically two different products that can form. These are isomers, and result from two pathways:



Which mechanism is followed more commonly comes from considering which pathway will give the most stable carbocation during the addition process. Alkyl groups around a carbocation stabilize it due to their **positive inductive effects**, meaning that they push electron density away from themselves, reducing the density of positive charge. In (a), the carbocation is a primary carbocation and is stabilized by only one such positive inductive effect, whereas the carbocation in (b) is a secondary carbocation in which there are two such effects and the stabilization is greater. Therefore, mechanism (b) is more likely, and 2-bromopropane forms more frequently than 1-bromopropane.

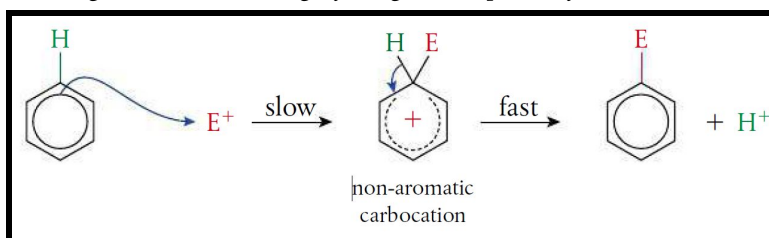


Markovnikov's rules can be used to predict the outcome of such reactions between unsymmetrical alkenes and hydrogen halides, stating that *the hydrogen will attach to the carbon that is already bonded to the greater number of hydrogens*.

Electrophilic substitution reactions: benzene

Despite its high unsaturation, benzene does not behave like alkenes in reactions. Its stable aromatic ring determines that substitution, not addition, is its favored reaction. Benzene is attractive to electrophiles because its ring is a region of electron density. Therefore the name electrophilic substitution.

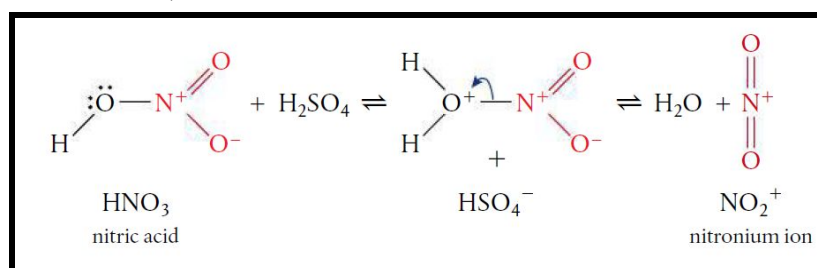
The mechanism of the electrophilic substitution reactions of benzene is similar to that with other electrophiles. The reaction has high E_a and so proceeds slowly. This is because the first step in the mechanism leads to a disruption of the symmetry delocalised system, and the unstable carbocation that forms has both the entering atom and leaving hydrogen temporarily bonded to the ring:



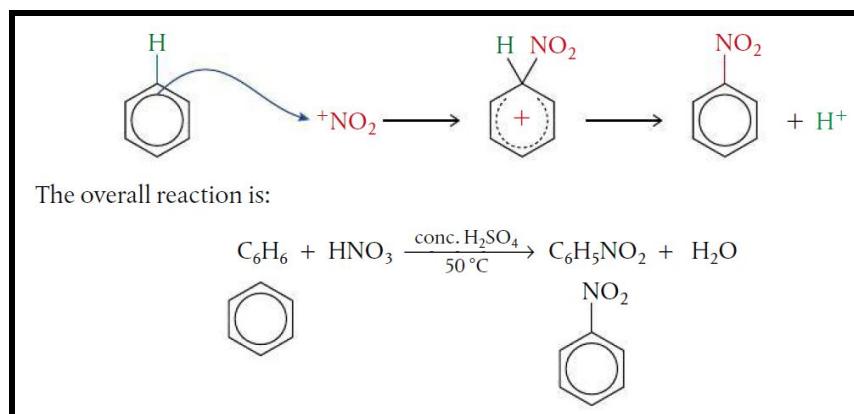
In the intermediate, the loss of symmetry is shown by the incomplete circle. But the loss of a hydrogen ion from this intermediate leads to the electrically neutral substitution as two electrons from the C-H bond move to regenerate the aromatic ring. This product is more stable.

Nitration of benzene (only benzene reaction that is required)

The nitration of benzene involves the substitution of -H with $-\text{NO}_2$ to form nitrobenzene $\text{C}_6\text{H}_5\text{NO}_2$. The electrophile in this mechanism, the nitronium ion (NO_2^+), is generated using a **nitrating mixture** consisting of concentrated nitric acid and concentrated sulfuric acid. Sulfuric acid, which is the stronger acid, protonates the nitric acid, which then loses a water molecule to form the nitronium ion:



NO_2^+ , the electrophile then follows the model mechanism described to form nitrobenzene:



Reduction reactions

Reduction of carbonyl compounds

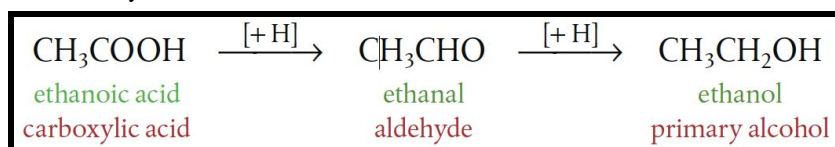
The oxidation of alcohols to carbonyl compounds takes place in the presence of a suitable oxidizing agent and yields different products depending on the alcohol and the conditions:

- Primary alcohol → Aldehyde → Carboxylic acid
- Secondary alcohol → Ketone

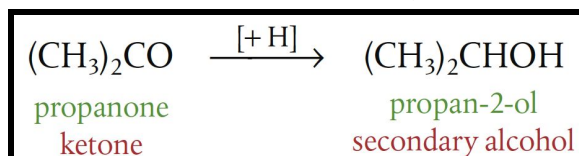
These reactions can be reversed using a suitable reducing agent:

- Sodium borohydride, NaBH_4 , in aqueous or alcoholic solution
- Lithium aluminium hydride, LiAlH_4 , in anhydrous conditions, such as dry ether followed by aqueous acid

Both these produce the hydride ion, H^- , which acts as a nucleophile on the electron deficient carbonyl carbon. NaBH_4 is the safer reagent, but it is not reactive enough to reduce carboxylic acids, so LiAlH_4 must be used for this. The symbol $[\text{+H}]$ can be used to show reduction, whereas $[\text{+O}]$ shows oxidation.



Conditions: LiAlH_4 in dry ether. Reaction doesn't stop at aldehyde as it reacts to readily with the LiAlH_4

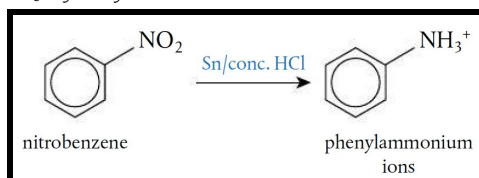


Conditions: Heat with NaBH_4

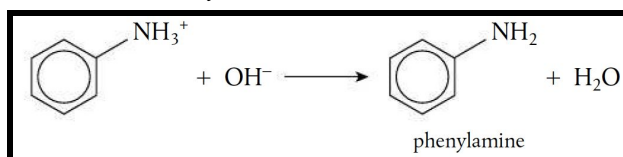
Reduction of nitrobenzene

Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be converted to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, in a two-step process.

- 1) $\text{C}_6\text{H}_5\text{NO}_2$ is heated under reflux with a mixture of tin, Sn, and concentrated HCl, producing phenylammonium ions, $\text{C}_6\text{H}_5\text{NH}_3^+$ (which are protonated due to acidic conditions):

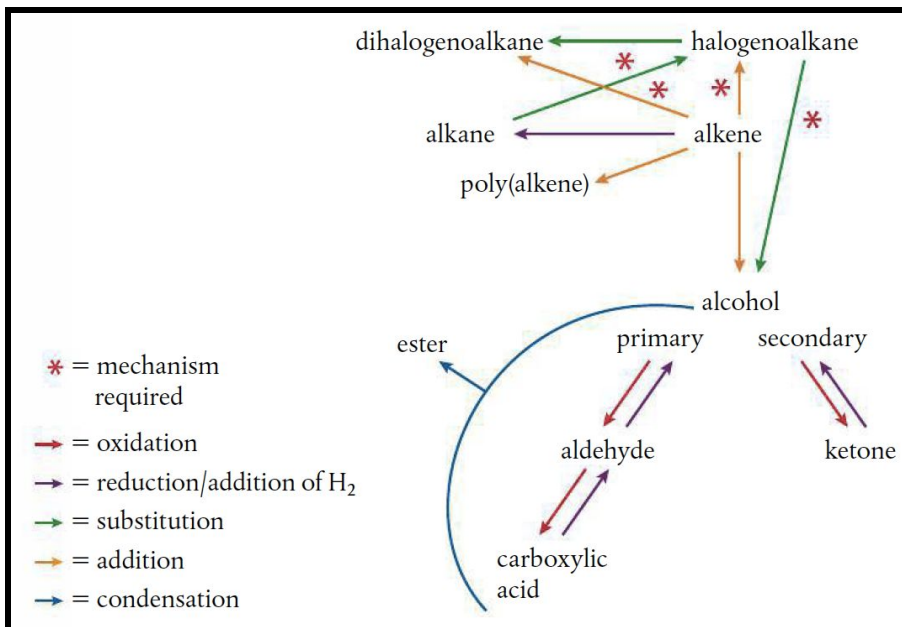


- 2) $\text{C}_6\text{H}_5\text{NH}_3^+$ is reacted with sodium hydroxide, NaOH , to remove the H^+ and form $\text{C}_6\text{H}_5\text{NH}_2$:



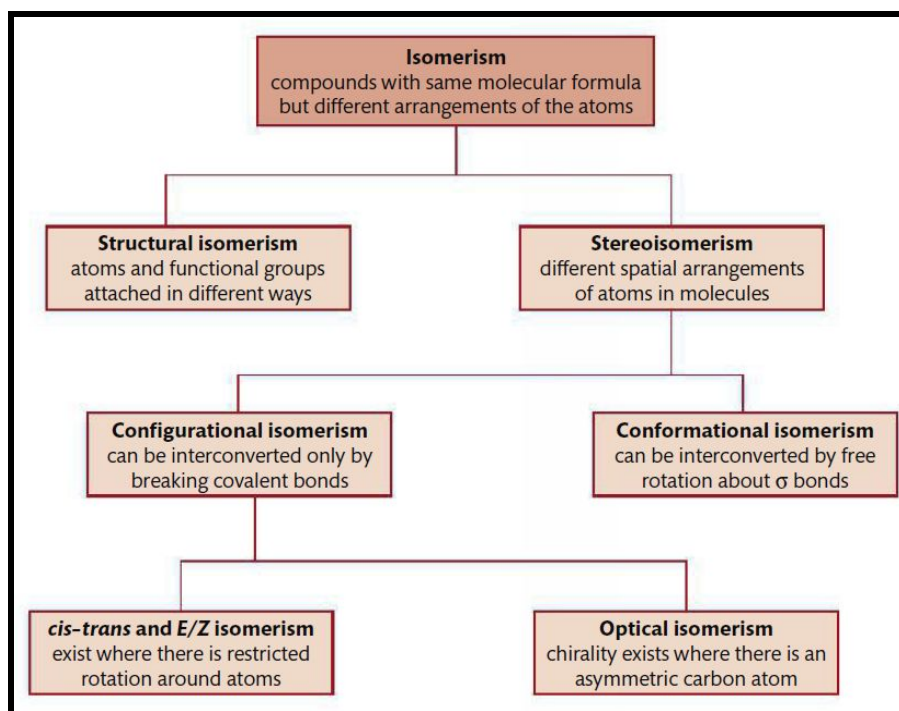
20.2 Synthetic routes

This section deals with how organic reactions are interrelated. This helps to synthesize routes to form compounds from those that are already available. Shown below is a chart relating common reactions:



The series of discrete steps involved in converting the starting material to the desired compound is the **synthetic route**. Retro-synthesis involves working backward from the **target molecule** to identify **precursors**, from which the optimal synthetic routes can be determined.

20.3 Stereoisomerism



Cis-trans and E/Z isomers

When there is some constraint in a molecule that restricts the free rotation of substituted groups, they become fixed in space relative to each other. In such cases, the position of the groups must be described with respect to a reference plane. There are two instances where such isomers arise:

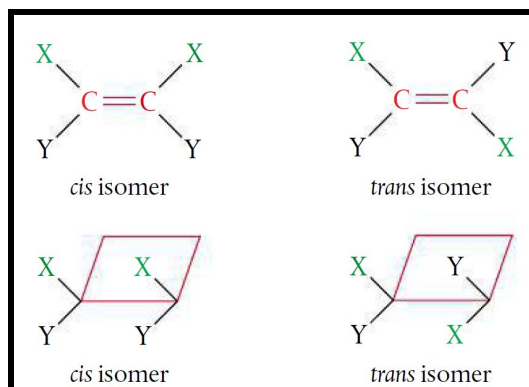
- **Double bonded molecules**

- Free rotation in a double bond is not possible as this would push the p orbitals out of position, causing the bond to break. The reference plane is perpendicular to the sigma bond and passes through the double bond.

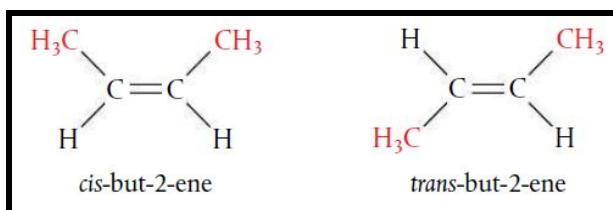
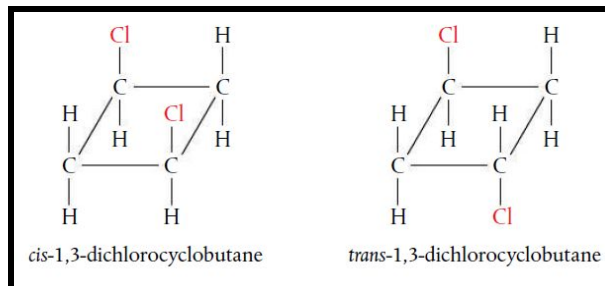
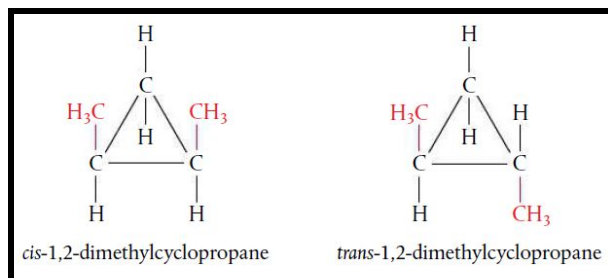
- **Cyclic molecules**

- Cycloalkanes contain a ring of C atoms that restricts rotation. The reference plane is the plane of the ring.

When the molecule contains two or more different groups attached to the double bond or to the ring, these can be arranged to give two different isomers. The simplest examples, including only two different substituents, form what are known as cis and trans isomers.



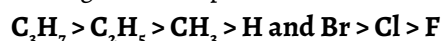
Cis refers to the isomer that has the same groups on the same side of the double bond or ring, while trans is the isomer that has the same groups on opposite sides, or across the reference plane. For eg:



When the carbon atoms of the double bond are bonded to more than two different substituents, the cis-trans designation breaks down. As all the groups attached to the C=C bond are different, there are no 'same groups' to position relative to the reference plane. For this E/Z isomerism is used, based on the Cahn-Ingold-Prelog rules of priority, which are applied in turn to the groups on each end of the bond:

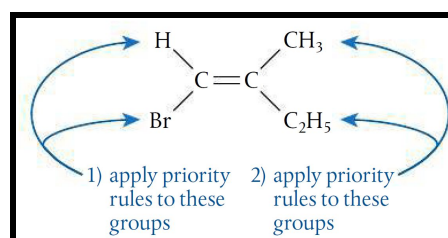
- 1) Look at the atom bonded to the carbon of the double bond. The atom with the higher atomic number has the higher priority
- 2) If the atoms are the same, for example if they are both carbon atoms, apply the same rule to the next bonded atom. This means that longer hydrocarbon chains have higher priority

Taking the example below:



Next the positions of the highest priority groups on the two carbons of the double bond are compared:

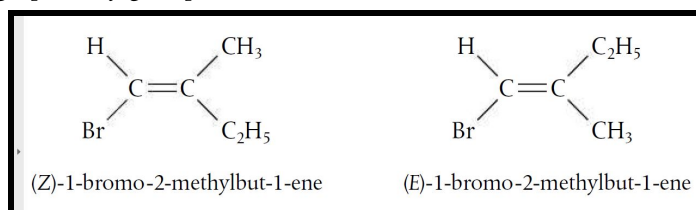
- If the two highest priority groups are on the same side of the C=C bond, then the isomer is Z
- If the two highest priority groups are on the opposite side of the C=C bond, then the isomer is E



Applying these rules to the example:

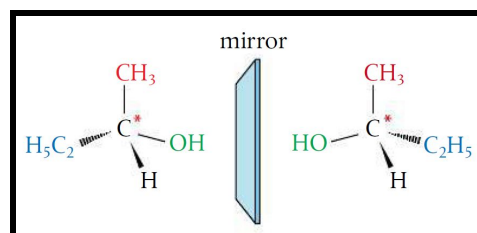
- Br has the higher priority of the groups attached to the left-hand carbon
- C_2H_5 has the higher priority of the two groups attached to the right-hand carbon

In the example, the high priority groups are on the same side, so it is the Z isomer. Comparing:



Optical isomers

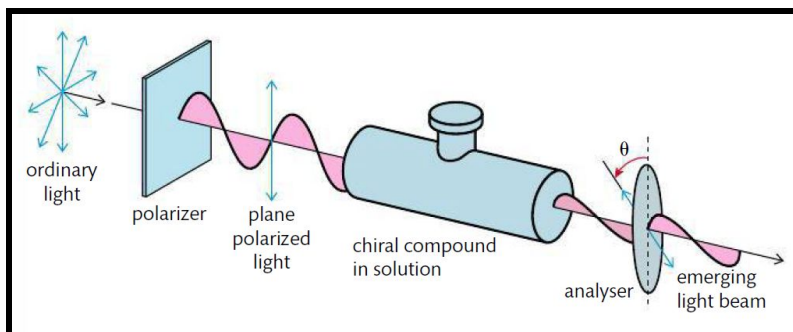
A C atom attached to four different atoms or groups is known as **chiral**. The four groups, arranged tetrahedrally around the C atom form bond angles of 109.5° , and can be arranged in two different 3D configurations which are mirror images of each other. This is optical isomerism, and the term refers to the ways in which the isomers interact with plane-polarized light.



The images of the two isomers are **non-superimposable**, with the two forms called **enantiomers**. A mixture containing equal amounts of the two enantiomers is known as a **racemic mixture**. In molecules with more than one chiral centre, each position can create different orientations. When molecules have different configurations at one or more, but not all chiral centres, they are **diastereomers**.

Properties of optical isomers

- Optical activity
 - Optical isomers show a difference in a specific interaction with light. Ordinary light consists of EM waves that oscillate in an infinite number of planes at right angles to the direction of travel. Passing such light through a polarizer results in polarized light, for which the electric field vector vibrates only in one plane.
 - When plane-polarized light is passed through a solution of optical isomers, they rotate the plane of polarization. The extent of this rotation is measured using a **polarimeter**.



When plane polarized light is passed through the solution of isomers, the plane of polarized light is rotated, before passing through an analyzer, which is rotated till light passes through it. This allows us to determine the extent and direction of rotation. When comparing different enantiomers at the same concentration, plane-polarized light is rotated by equal amounts but in different directions. However, racemic mixture does not rotate light and is said to be optically inactive (equal amounts of both enantiomers cancel out the two effects).

- Reactivity with other chiral molecules
 - When a racemic mixture is reacted with a single enantiomer of another chiral compound, the two components react to produce different products. These products have distinct chemical and physical properties and so can be separated from each other relatively easily by a process known as **resolution**.