Organic Chemistry SL (answers)

IB CHEMISTRY SL

25	16		6	2	25
Mn	S	J	C	He	Mn
Manganese	Sulfur		Carbon	Helium	Manganese
54.938045	32.065		12.0107	4.002602	54.938045

10.1 Fundamentals of organic chemistry

Understandings:

- A homologous series is a series of compounds of the same family, with the same general formula, which differ from each other by a common structural unit.
- Structural formulas can be represented in full and condensed format.
- Structural isomers are compounds with the same molecular formula but different arrangements of atoms.
- Functional groups are the reactive parts of molecules.
- Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds.
- Benzene is an aromatic, unsaturated hydrocarbon.

Applications and skills:

- Explanation of the trends in boiling points of members of a homologous series.
- Distinction between empirical, molecular and structural formulas
- Identification of different classes: alkanes, alkenes, alkynes, halogenoalkanes, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, amines, amides, nitriles and arenes.
- Identification of typical functional groups in molecules eg phenyl, hydroxyl, carbonyl, carboxyl, carboxamide, aldehyde, ester, ether, amine, nitrile, alkyl, alkenyl and alkynyl.
- Construction of 3-D models (real or virtual) of organic molecules.
- Application of IUPAC rules in the nomenclature of straight-chain and branched- chain isomers.
- Identification of primary, secondary and tertiary carbon atoms in halogenoalkanes and alcohols and primary, secondary and tertiary nitrogen atoms in amines.
- Discussion of the structure of benzene using physical and chemical evidence.

Guidance:

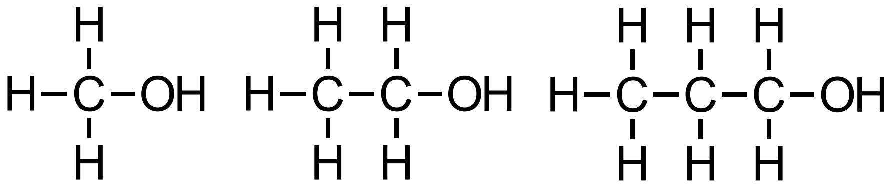
- Skeletal formulas should be discussed in the course.
- The general formulas (eg C_nH_{2n+2}) of alkanes, alkenes, alkynes, ketones, alcohols, aldehydes and carboxylic acids should be known.
- The distinction between class names and functional group names needs to be made. Eg for OH, hydroxyl is the functional group whereas alcohol is the class name.
- The following nomenclature should be covered:
    - non-cyclic alkanes and halogenoalkanes up to halohexanes.
    - alkenes up to hexene and alkynes up to hexyne.
    - compounds up to six carbon atoms (in the basic chain for nomenclature purposes) containing only one of the classes of functional groups: alcohols, ethers, aldehydes, halogenoalkanes, ketones, esters and carboxylic acids.

Syllabus objectives

Objective	I am confident with this	I need to review this	I need help with this
Outline the features of a homologous series			
Identify different functional groups within a molecule			
Identify organic compounds from the different types of structural formulae			
Apply IUPAC rules to name organic compounds			
Classify organic compounds as primary, secondary or tertiary			
Explain the trends in boiling points of a homologous series			
Outline the physical and chemical evidence for the structure of benzene			

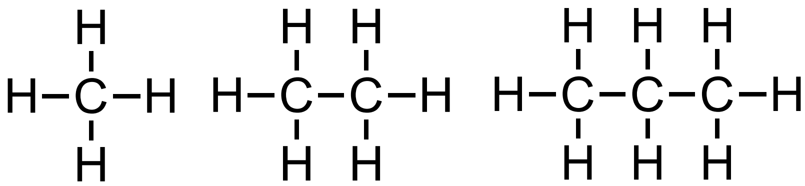
Homologous series

- A homologous series is a series of organic compounds of the same family which differ by a common structural unit (CH_2).



- Functional group: hydroxyl (OH) – each member differs by a CH_2 group.

- Members of a homologous series have similar chemical properties.



- They also show a gradation in physical properties (such as the increasing boiling point of the alkanes).

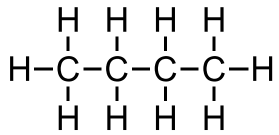
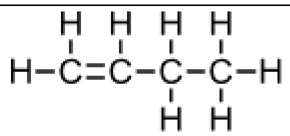
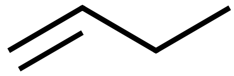
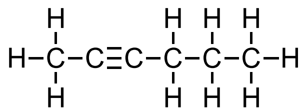
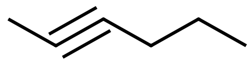
- They also have the same general formula (C_nH_{2n+2}).

Summary:

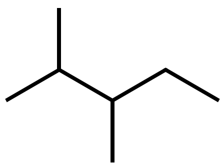
Members of a homologous series:

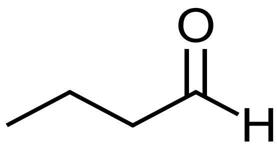
- differ by a CH_2
- have the same general formula
- have similar chemical properties
- show a gradation (gradual increase) in physical properties such as boiling point

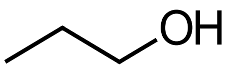
Structural formulae

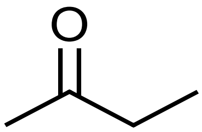
Compound	Molecular formula	Empirical formula	Full structural formula	Condensed structural formula	Skeletal formula
butane	C_4H_{10}	C_2H_5		$CH_3(CH_2)_2CH_3$	
but-1-ene	C_4H_8	CH_4		$CH_2CHCH_2CH_3$	
hex-2-yne	C_6H_{10}	C_3H_5		$CH_3CCCH_2CH_2CH_3$	

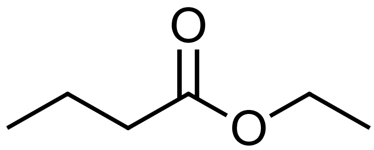
Skeletal formulae



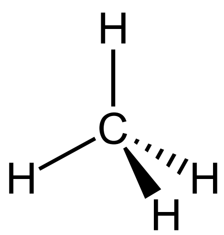








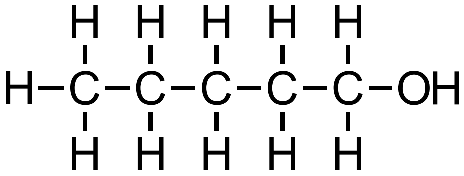
Stereochemical formulae



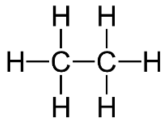
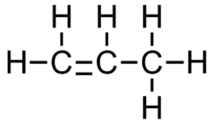
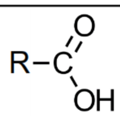
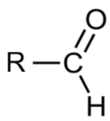
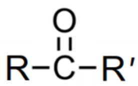
- The two solid lines are in the plane of the paper.
- The wedge is coming out from the plane of the paper.
- The dashed line is going into the plane of the paper.

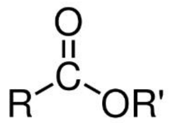
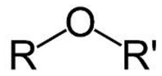
Functional groups

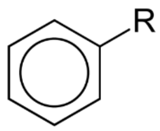
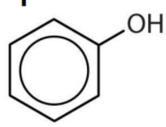
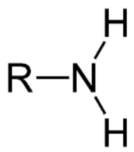
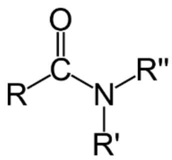
- A functional group is a group of atoms within a molecule that are responsible for the characteristic chemical reactions of the molecule.



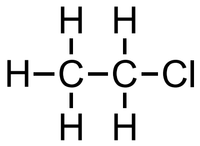
Class: alcohols
Functional group: hydroxyl group

Class	Functional group	Example
alkane	 alkyl	ethane CH_3CH_3
alkene	 alkenyl	propene CH_3CHCH_2
alkyne	H−C≡C−H alkynyl	ethyne CHCH
alcohol	R-OH hydroxyl	methanol CH_3OH
carboxylic acid	 carboxyl	propanoic acid CH_3CH_2COOH
aldehyde	 aldehyde	ethanal CH_3CHO
ketone	 ketone	butanone $CH_3COCH_2CH_3$

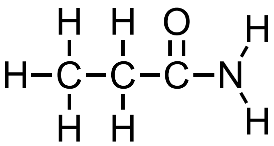
ester		ethyl ethanoate $CH_3COOCH_2CH_3$
ether		methoxymethane H_3COCH_3
nitrile	$R-C\equiv N$	butanenitrile $CH_3CH_2CH_2CN$
halogenoalkane	R-X halogeno	chloroethane CH_3Cl

arene	 phenyl	phenol 
amine		ethanamine $CH_3CH_2NH_2$
amide	 carboxamide	propanamide $CH_3CH_2CONH_2$

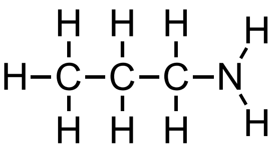
Answers:



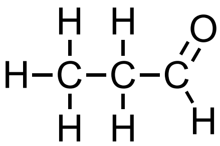
Class: halogenoalkane
Functional group: halogeno



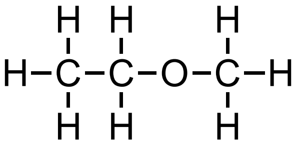
Class: amide
Functional group: carboxamide



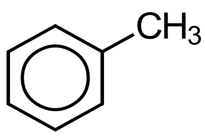
Class: amine
Functional group: amine



Class: aldehyde
Functional group: aldehyde



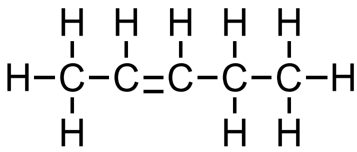
Class: ether
Functional group: ether



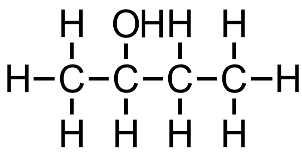
Class: arene
Functional group: phenyl

$H-C\equiv C-H$

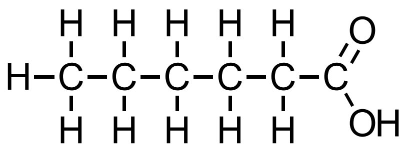
Class: alkyne
Functional group: alkynyl



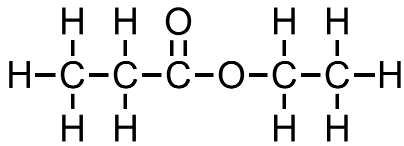
Class: alkene
Functional group: alkenyl



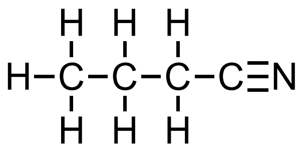
Class: alcohol
Functional group: hydroxyl



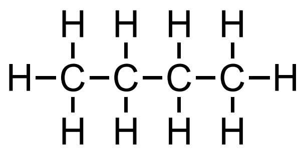
Class: carboxylic acid
Functional group: carboxyl



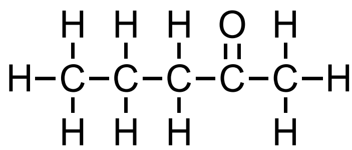
Class: ester
Functional group: ester



Class: nitrile
Functional group: nitrile



Class: alkane
Functional group: alkyl



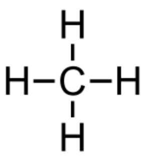
Class: ketone
Functional group: ketone

Naming organic compounds

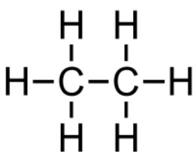
- Students are required to name organic compounds with up to 6 carbon atoms.

number of carbon atoms	root / stem
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-

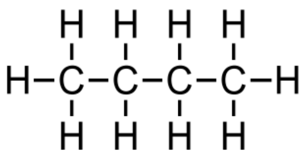
Alkanes



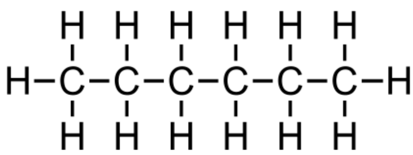
Methane



Ethane



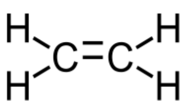
Butane



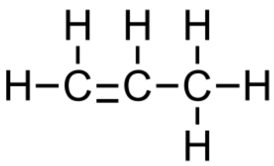
Hexane

- General formula C_nH_{2n+2}
- Alkanes are saturated hydrocarbons (C-C single bonds)

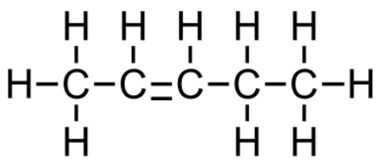
Alkenes



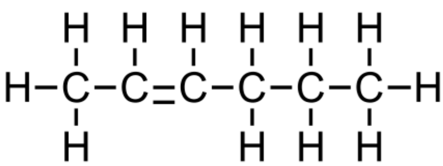
Ethene



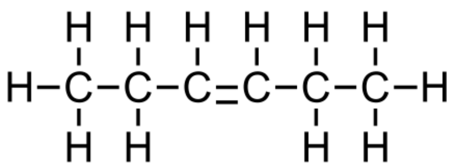
Propene



Pent-2-ene



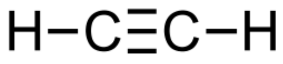
Hex-2-ene



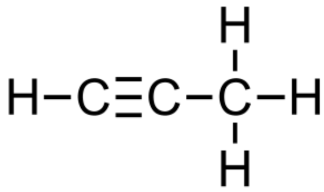
Hex-3-ene

- General formula C_nH_{2n}
- Alkenes are unsaturated hydrocarbons (C=C double bond)

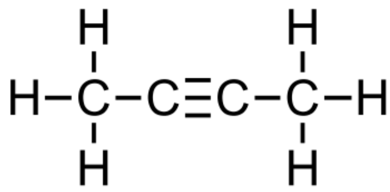
Alkynes



Ethyne



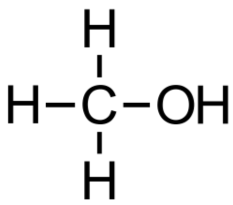
Propyne



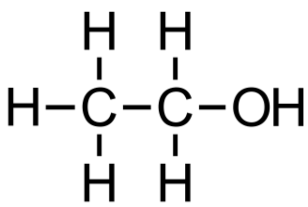
But-2-yne

- General formula C_nH_{2n-2}
- Alkynes are unsaturated hydrocarbons (C to C triple bond)

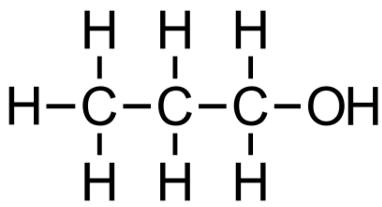
Alcohols



Methanol



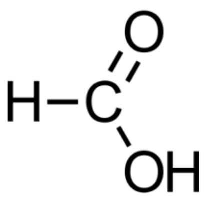
Ethanol



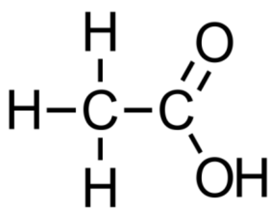
Propan-1-ol

- General formula $C_nH_{2n+1}OH$

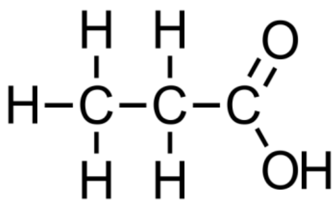
Carboxylic acids



Methanoic acid



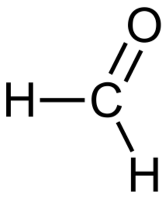
Ethanoic acid



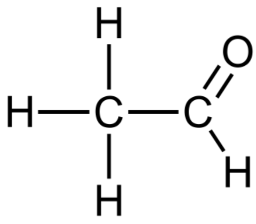
Propanoic acid

- General formula $C_nH_{2n+1}COOH$

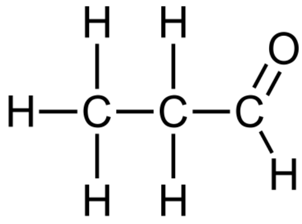
Aldehydes



Methanal

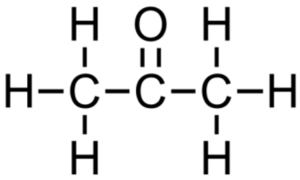


Ethanal

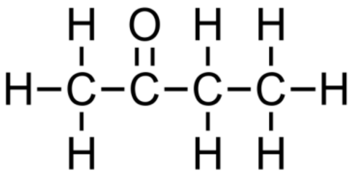


Propanal

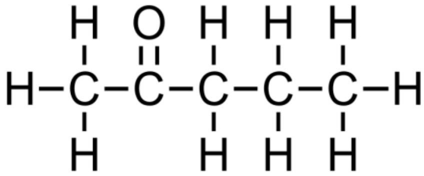
Ketones



Propanone



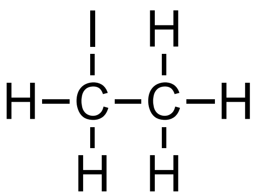
Butanone



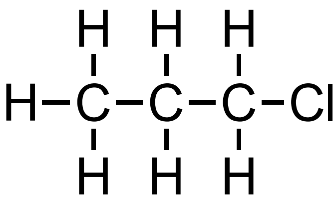
Pentan-2-one

Halogenoalkanes

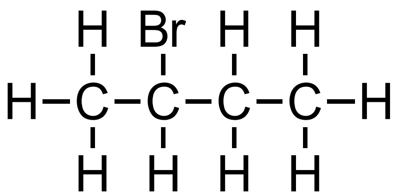
- Halogenoalkanes contain an atom of fluorine, chlorine, bromine or iodine.
- General formula $C_nH_{2n+1}X$



Iodoethane



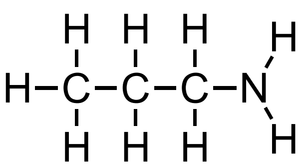
1-chloropropane



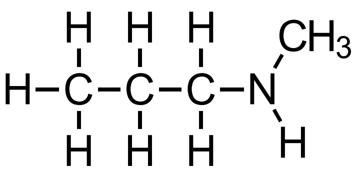
2-bromobutane

Amines

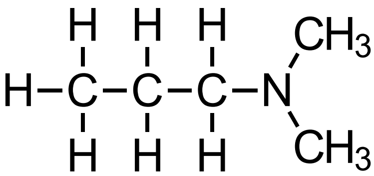
- Amines are derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group.



Propanamine

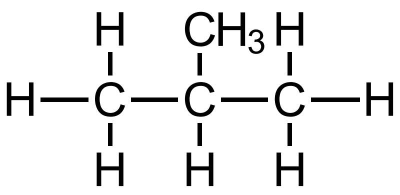


N-methylpropanamine

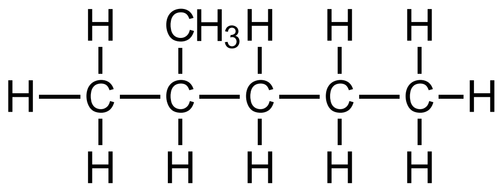


N,N-dimethylpropanamine

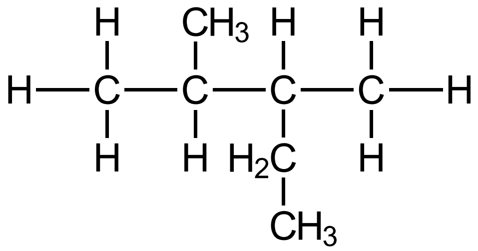
Branched alkanes



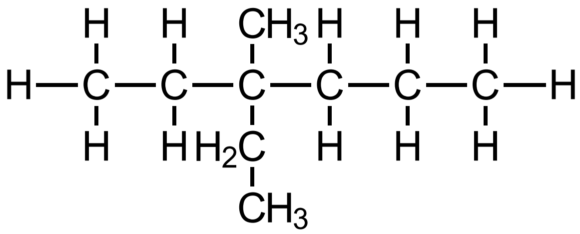
2-methylpropane



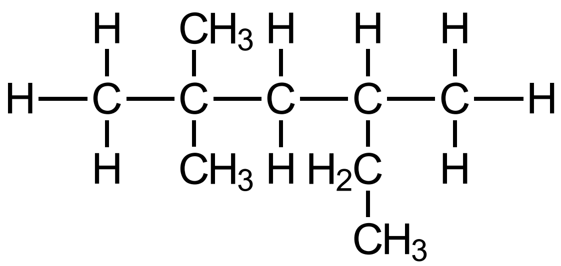
2-methylpentane



2,3-dimethylpentane



3-ethyl-3-methylhexane

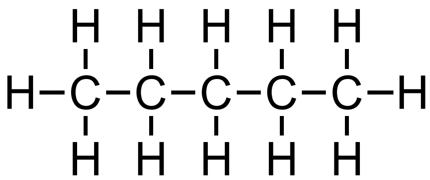


2,2,4-trimethylhexane

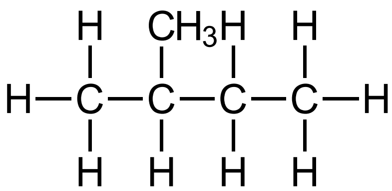
Structural isomers

- Structural isomers are compounds with the same molecular formula but different arrangements of atoms.

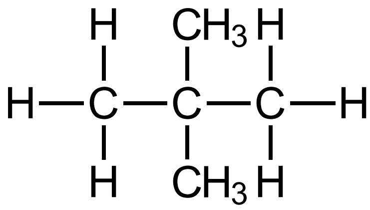
Structural isomers of C_5H_{12}



Pentane



2-methylbutane

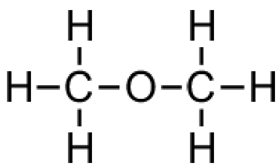


2,2-dimethylpropane

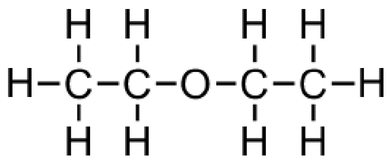
Ethers

- Ethers have the ether functional group R-O-R’, where R can be the same or different.
- Ethers are weakly polar molecules due to the C-O-C bond
- They have quite low boiling points: CH_3OCH_3 boils at -24^oC
- Ethers with up to 3 carbon atoms are soluble in water but the solubility decreases with increasing number of carbon atoms.

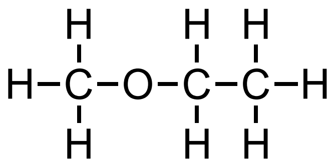
Exercise: Name the following ethers:



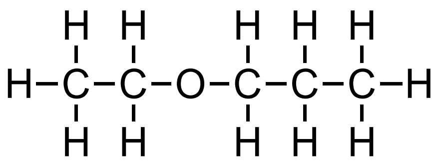
Methoxymethane



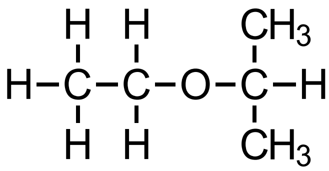
Ethoxyethane



Methoxyethane



1-ethoxypropane

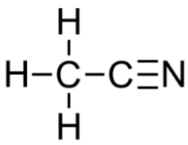


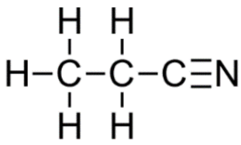
2-exothypropane

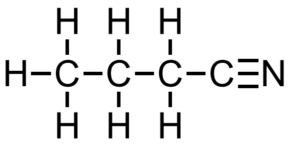
Nitriles

- Nitriles have the functional group −C≡N
- Nitriles cannot form hydrogen bonds, however, they do have quite high boiling points: CH_3CN boils at 83 ^oC.
- Ethanenitrile is soluble in water but solubility decreases with increasing carbon chain length.

Exercise: Name the following nitriles:





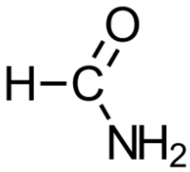


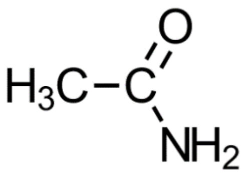
Ethanenitrile **Propanenitrile** **Butanenitrile**

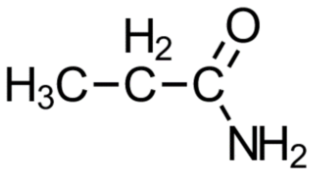
Amides

- Amides are derivatives of carboxylic acids in which the OH has been replaced by a NH_2.
- Amides contain the carboxamide functional group R-$CONH_2$
- They have high boiling points as they are able to form hydrogen bonds between molecules.
- They are also soluble in water as they are able to form hydrogen bonds with water molecules.

Exercise: Name the following amides:



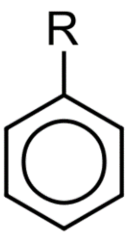




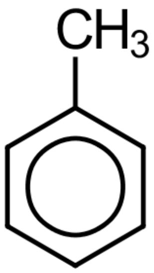
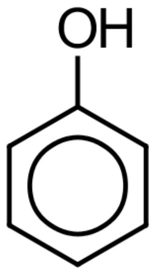
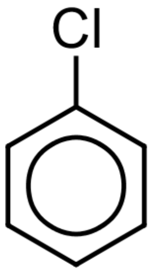
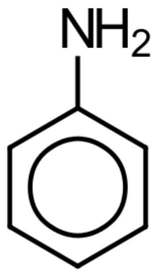
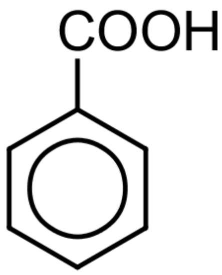
Methanamide **Ethanamide** **Propanamide**

Arenes

- Arenes contain the phenyl functional group.
- The phenyl functional group is a cyclic ring composed of 6 carbon atoms and 5 hydrogen atoms (C_6H_5-).



- Examples of molecules with the phenyl functional group are shown below.

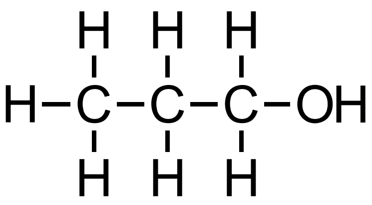
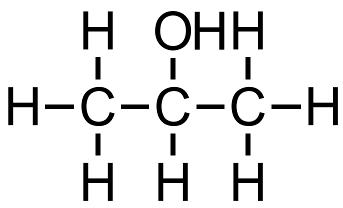
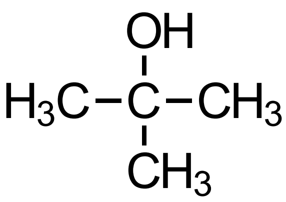







Benzene **Methylbenzene** **Phenol** **Chlorobenzene** **Phenylamine** **Benzoic acid**

Hydroxybenzene **Aniline** **Benzenecarboxylic acid**

Classification of organic compounds

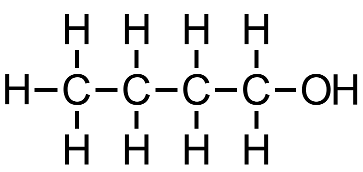
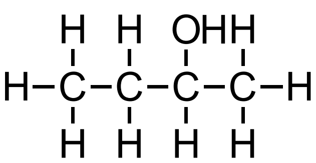
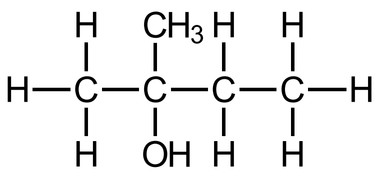
- Alcohols and halogenoalkanes can be classified as primary, secondary or tertiary depending on how many carbons atoms are bonded to the carbon atom that is bonded directly to the functional group.

Ethanol (primary) **Propan-2-ol (secondary)** **2-methylpropan-2-ol (tertiary)**

Exercises:

1) Name and classify the following alcohols as primary, secondary or tertiary:

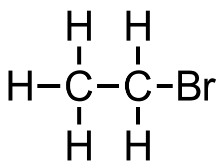




Butan-1-ol
Primary alcohol

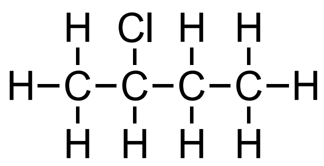
Butan-2-ol
Secondary alcohol

2-methylbutan-2-ol
Tertiary alcohol

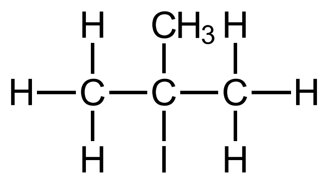
2) Name and classify the following halogenoalkanes as primary, secondary or tertiary:



Bromoethane
Primary halogenoalkane

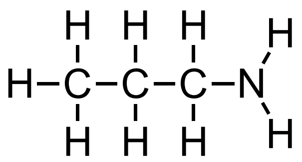


2-chlorobutane
Secondary halogenoalkane

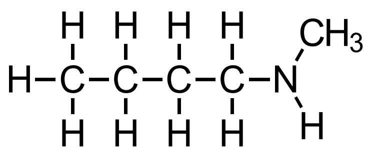


2-iodo-2-methylpropane
Tertiary halogenoalkane

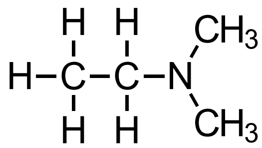
3) Name and classify the following amines as primary, secondary or tertiary:



Propanamine
Primary amine



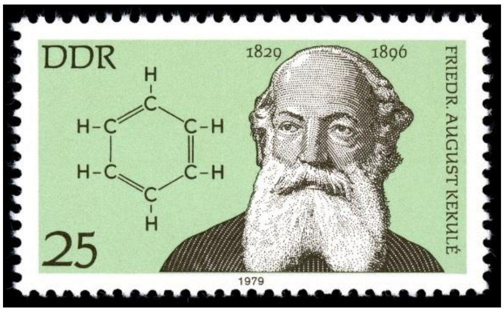
N-methylbutanamine
Secondary amine



N,N-dimethylethanamine
Tertiary amine

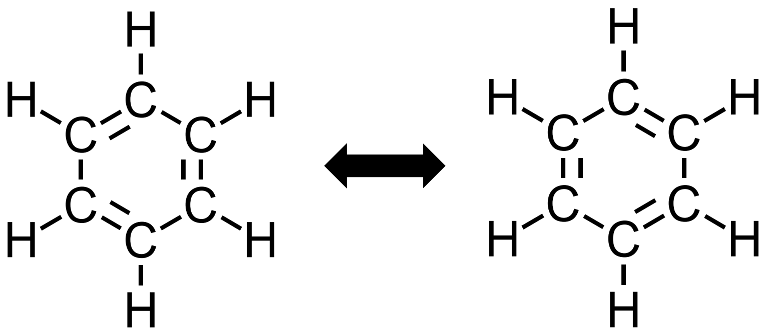
Evidence for the structure of benzene

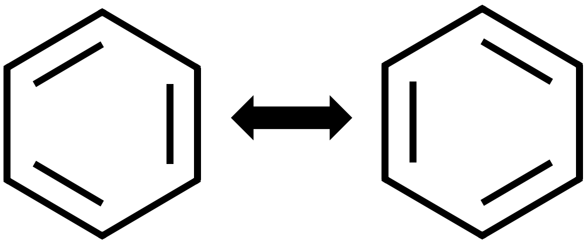
- Benzene is an aromatic unsaturated hydrocarbon
- Molecular formula C_6H_6
- Empirical formula CH



In 1865 Friedrich August Kekulé suggested that benzene contained a ring of six carbon atoms with alternating single and double bonds.

- The Kekulé structure of benzene consists of alternating single and double bonds.





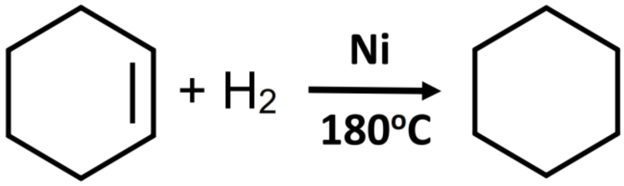
How do we know that the structure of benzene does not consist of alternating single and double bonds?

The length of the strength of the C to C bonds (physical evidence)

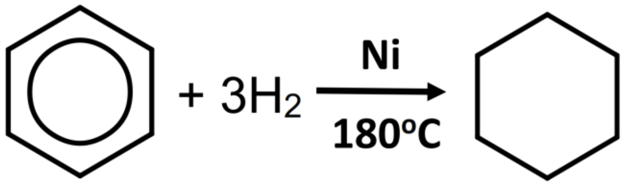
- The C to C bonds are of identical length and strength.

- The length and strength of the C to C bonds in benzene are intermediate between a single and a double bond.

The enthalpy of hydrogenation of benzene is less than predicted (chemical evidence)



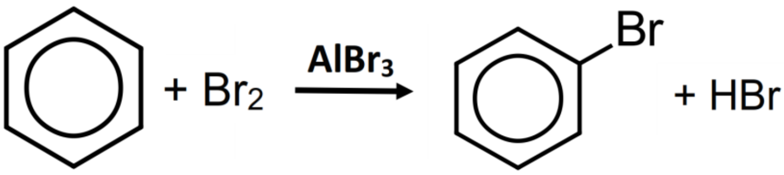
ΔH = -120 kJ mol^{-1}



ΔH = -210 kJ mol^{-1}

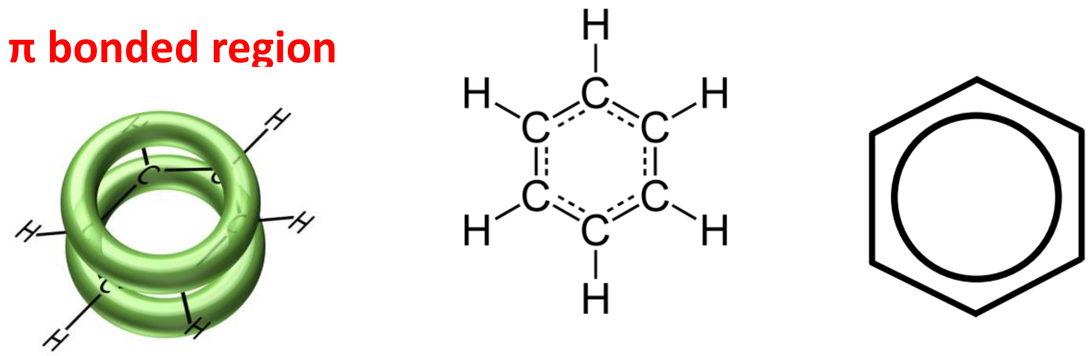
- Delocalization of π electrons minimizes the repulsion between the electrons, lowering the internal energy by 150 kJ mol^{-1} (resonance energy).

Benzene undergoes substitution reactions, rather than addition reactions (chemical evidence)



The actual structure of benzene

- Benzene has delocalised π electrons in the pi bond region.



- Each carbon to carbon bond is identical - intermediate in strength and length between a single and a double bond.

Factors that affect the boiling points of organic compounds

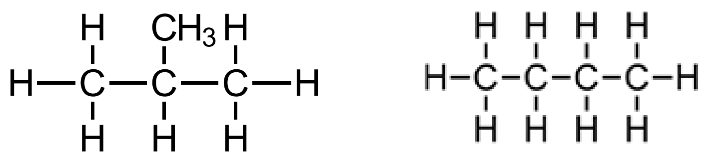
Molar mass and boiling point

alkane	molar mass ($gmol^{-1}$)	boiling point (°C)
methane	16	-164
ethane	30	-89
propane	44	-42
butane	58	-0.5
pentane	72	36
hexane	86	69
heptane	100	98
octane	114	125
nonane	128	151
decane	142	174

- As the molar mass of the compound increases, the boiling point increases.
- As the molar mass increases, the strength of the London dispersion forces between the molecules increases (the molecules have more electrons and are more easily polarisable).
- More energy is required to overcome the London dispersion forces between the molecules, therefore, the boiling point increases.

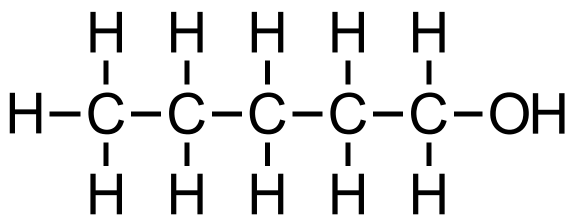
Branched chain isomers vs straight chain isomers

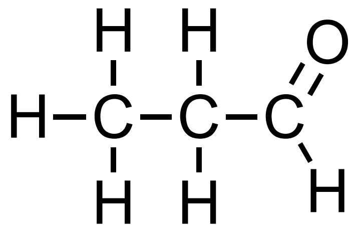
- Branched-chain isomers have lower boiling points than straight-chain isomers.
- The branches reduce the contact surface area between the molecules which reduces the strength of the London dispersion forces between the molecules and lowers the boiling point.
- The structures of 2-methylpropane (boiling point -11.7 °C) and butane (boiling point -1 °C) are shown below.



- 2-methylpropane, a branched alkane, has a lower boiling than butane.
- The branches result in a lower contact surface area between the molecules.

Effect of functional group





- Compounds with functional group containing H bonded to O or N have hydrogen bonding between their molecules.
- Compounds with functional group containing carbonyl group (C=O) have dipole-dipole forces between their molecules.
- Alcohols, amides and carboxylic acids have higher boiling points as they are able to form hydrogen bonds between their molecules.
- Aldehydes, ketones, and esters have dipole-dipole forces between their molecules.
- Alkanes, alkenes and alkynes have London dispersion forces between their molecules.

Amides — **low volatility**

Carboxylic acids

Alcohols

Ketones — **Increasing boiling point** ↑

Aldehydes

Esters

Alkanes — **high volatility**

Exercises:

1. Methane and heptane belong to the same class (the alkanes). Predict and explain which compound has a higher boiling point.
   Heptane has a larger molar mass than methane and therefore stronger London dispersion forces between the molecules and a higher boiling point.

2. Explain the difference in boiling point between the structural isomers pentane and 2-methylbutane.

   2-methylbutane, a branched hydrocarbon, has a lower boiling point than pentane. Branched hydrocarbons have weaker London dispersion forces between the molecules and lower boiling points because of the lower contact surface area.

3. Ethanol and propane have similar molar masses but different boiling points. Predict and explain which compound has the highest boiling point.
   Although they have similar molar masses, ethanol is able to form hydrogen bonds between its molecules whereas propane only has weaker London dispersion forces between the molecule and a lower boiling point.

10.2 Functional group chemistry

Understandings:

Alkanes:

- Alkanes have low reactivity and undergo free-radical substitution reactions.

Alkenes:

- Alkenes are more reactive than alkanes and undergo addition reactions.
- Bromine water can be used to distinguish between alkenes and alkanes.

Alcohols:

- Alcohols undergo nucleophilic substitution reactions with acids (also called esterification or condensation) and some undergo oxidation reactions.

Halogenoalkanes:

- Halogenoalkanes are more reactive than alkanes. They can undergo (nucleophilic) substitution reactions. A nucleophile is an electron-rich species containing a lone pair that it donates to an electron-deficient carbon.

Polymers:

- Addition polymers consist of a wide range of monomers and form the basis of the plastics industry.

Benzene:

- Benzene does not readily undergo addition reactions but does undergo electrophilic substitution reactions.

Applications and skills:

Alkanes:

- Writing equations for the complete and incomplete combustion of hydrocarbons.
- Explanation of the reaction of methane and ethane with halogens in terms of a free-radical substitution mechanism involving photochemical homolytic fission.

Alkenes:

- Writing equations for the reactions of alkenes with hydrogen and halogens and of symmetrical alkenes with hydrogen halides and water.
- Outline of the addition polymerisation of alkenes.
- Relationship between the structure of the monomer to the polymer and repeating unit.

Alcohols:

- Writing equations for the complete combustion of alcohols.
- Writing equations for the oxidation reactions of primary and secondary alcohols (using acidified potassium dichromate(VI) or potassium manganate(VII) as oxidizing agents).
- Explanation of distillation and reflux in the isolation of the aldehyde and carboxylic acid products.
- Writing the equation for the condensation reaction of an alcohol with a carboxylic acid, in the presence of a catalyst (eg concentrated sulfuric acid) to form an ester.

Halogenoalkanes:

- Writing the equation for the substitution reactions of halogenoalkanes with aqueous sodium hydroxide.

Guidance:

- Reference should be made to initiation, propagation and termination steps in free-radical substitution reactions. Free radicals should be represented by a single dot.
- The mechanisms of S_N1 and S_N2 and electrophilic substitution reactions are not required.

Syllabus objectives

Objective	I am confident with this	I need to review this	I need help with this
Outline the difference between homolytic and heterolytic bond fission			
Explain the lack of reactivity of the alkanes			
Write equations for the complete and incomplete combustion of alkanes			
Write equations for the free radical substitution reactions of methane and ethane with the halogens			
Write equations for the reactions of alkenes with hydrogen and halogens and of symmetrical alkenes with hydrogen halides and water			
Outline the test for unsaturation			
Outline addition polymerisation reactions of the alkenes			
Relate the structure of the monomer to the polymer and repeating unit			
Write equations for the complete combustion of alcohols			
Write equations for the oxidation reactions of primary and secondary alcohols			
Explain the use of distillation and reflux in the isolation of the aldehyde and carboxylic acid products			
Write equations for the condensation reaction of an alcohol with a carboxylic acid, to form an ester			
Write equations for the substitution reactions of halogenoalkanes with aqueous sodium hydroxide			
Outline the reactions of benzene			

Homolytic and heterolytic bond fission

- In homolytic bond fission, a covalent bond between two atoms in a molecule breaks with each atom taking one electron from the bond.

$$X:Y \rightarrow X\cdot + Y\cdot$$

- Homolytic bond fission results in the formation of free radicals (radicals) - highly reactive species with unpaired electrons.

- In heterolytic bond fission, a covalent bond between two atoms in a molecule breaks with one atom taking both bonding electrons.

$$X:Y \rightarrow X:^{-} + Y^{+}$$

- Heterolytic bond fission results in the formation of ions (cation and anion). The more electronegative atom usually takes both bonding electrons.

Exercise: Outline the difference between homolytic and heterolytic bond fission.

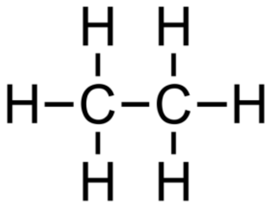
Homolytic bond fission results in the formation of free-radicals.

Heterolytic bond fission results in the formation of ions.

Reactions of the alkanes

- Alkanes have low reactivity for two reasons:

1. the C-H bond is a non-polar bond.



2. the C-C and C-H bonds are relatively strong (C-C 348 kJ mol^{-1} C-H 412 kJ mol^{-1}).

- Alkanes undergo two types of reactions: combustion and free radical substitution reactions.

Combustion reactions of the alkanes

- Alkanes can undergo complete combustion or incomplete combustion, depending how much oxygen is available.
- Complete combustion occurs when alkanes are burned in excess oxygen.
- The products are carbon dioxide and water.

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

- Incomplete combustion occurs in a lack of oxygen (not enough oxygen).
- Products are either carbon monoxide or carbon and water.

$$C_3H_{8(g)} + 3\tfrac{1}{2}O_{2(g)} \rightarrow 3CO_{(g)} + 4H_2O_{(g)}$$

$$C_3H_{8(g)} + 2O_{2(g)} \rightarrow 3C_{(s)} + 4H_2O_{(g)}$$

Exercise:

1. Outline the difference between complete and incomplete combustion.

   Complete combustion occurs in an excess of oxygen - the product is CO_2

   Incomplete combustion occurs in a lack of oxygen – the product is CO

2. Write equations for the complete and incomplete combustion of butane (C_4H_{10}).

   C_4H_{10} (g) + 6½O_2 (g) → 4CO_2 (g) + 5H_2O (l)

   C_4H_{10} (g) + 4½O_2 (g) → 4CO (g) + 5H_2O (l)

Free-radical substitution reactions of the alkanes

- Alkanes undergo free-radical substitution reactions which take place in three stages: initiation, propagation and termination.

Initiation – occurs in the presence of UV light

$$Cl_2 \xrightarrow{UV} 2Cl\bullet$$

- Photochemical homolytic bond fission – the bond between the chlorine atoms is split by UV light with each chlorine atom taking one electron from the single bond.

Propagation – keeps the reaction going

$$CH_4 + Cl\bullet \rightarrow CH_3\bullet + HCl$$

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

Termination – ends the reaction.

- The free radicals pair up to form compounds.

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

$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$$

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$

- Overall equation for the reaction is:

$$CH_{4(g)} + Cl_{2(g)} \xrightarrow{UV} CH_3Cl_{(g)} + HCl_{(g)}$$

Exercise: Ethane reacts with bromine to form bromoethane in a free-radical substitution reaction. Write initiation, propagation and termination steps for the reaction.

Initiation (occurs in the presence of UV)

$Br_2 \rightarrow 2Br\bullet$

Propagation reactions:

$Br\bullet + C_2H_6 \rightarrow C_2H_5\bullet + HBr$
$C_2H_5\bullet + Br_2 \rightarrow C_2H_5Br + Br\bullet$

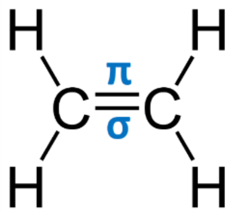
Termination reactions:
$C_2H_5\bullet + C_2H_5\bullet \rightarrow C_4H_{10}$

$Br\bullet + Br\bullet \rightarrow Br_2$

$C_2H_5\bullet + Br\bullet \rightarrow C_2H_5Br$

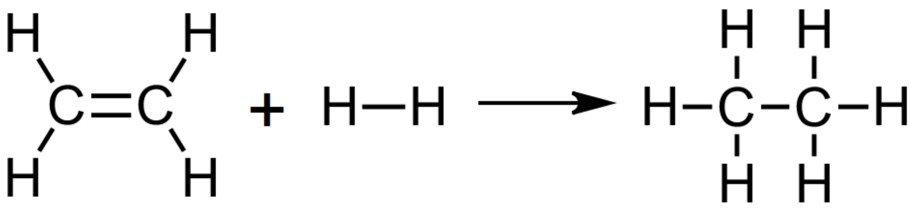
Reactions of the alkenes

- Alkenes undergo addition reactions.
- Alkenes are reactive as the π bond is easily broken to form two new bonding positions.



Hydrogenation

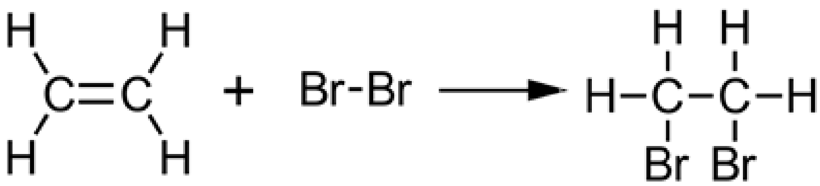
- Alkenes react with hydrogen in the presence of a nickel catalyst at a temperature of 150 ^{o}C to form alkanes.



$$C_2H_{4(g)} + H_{2(g)} \xrightarrow{\text{Ni } 150^{o}\text{C}} C_2H_{6(g)}$$

Halogenation

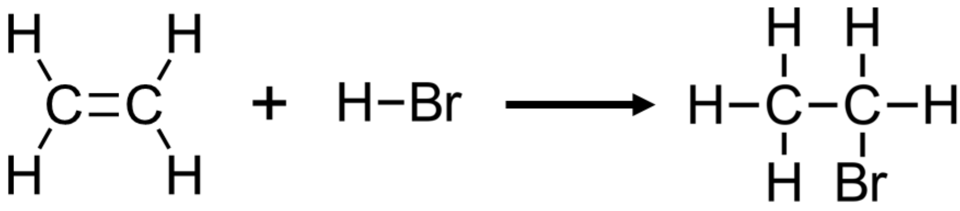
- Alkenes react with halogens to produce dihalogeno compounds.



$$C_2H_{4(g)} + Br_{2(g)} \longrightarrow CH_2BrCH_2Br_{(g)}$$

- The colour change in this reaction is brown to colourless (the bromine water is decolourised).
- This colour change indicates the presence of carbon to carbon double bonds (unsaturation).

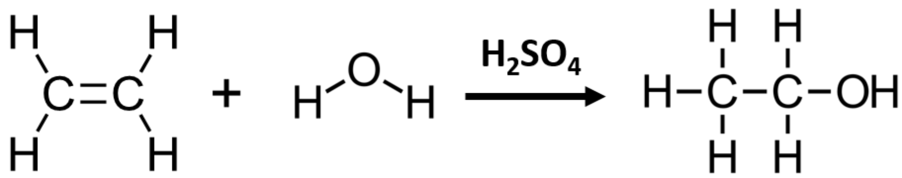
- Alkenes react with hydrogen halides (HCl, HBr and HI) to produce halogenoalkanes.



$$C_2H_{4(g)} + HBr_{(g)} \longrightarrow CH_3CH_2Br_{(g)}$$

Hydration

- Alkenes react with steam in the presence of a sulfuric acid catalyst to form alcohols.

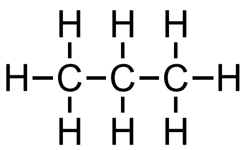


$$C_2H_{4(g)} + H_2O_{(g)} \xrightarrow{H_2SO_4} CH_3CH_2OH_{(l)}$$

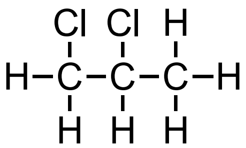
Exercises:

1) Draw structural formulae for the products of the following reactions:

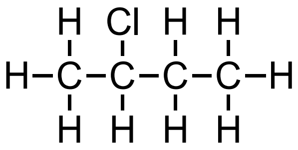
a)



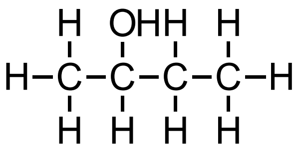
b)



c)



d)



2) For each of the above reactions, write balanced equations, state the conditions (including catalysts) and name the product formed.

a) $CH_2CHCH_{3(g)} + H_{2(g)} \rightarrow CH_3CH_2CH_{3(g)}$ (propane)

Conditions: Nickel (Ni) catalyst at 150^{o}C, high temperature and pressure

b) $CH_2CHCH_{3(g)} + Cl_{2(g)} \rightarrow CH_2ClCHClCH_{3(g)}$ (1,2-dichloropropane)

c) $CH_3CHCHCH_{3(g)} + HCl_{(g)} \rightarrow CH_3CHClCH_2CH_{3(g)}$ (2-chlorobutane)

d) $CH_3CHCHCH_{3(g)} + H_2O_{(g)} \rightarrow CH_3CH(OH)CH_2CH_{3\,(l)}$ (butan-2-ol)

Conditions: react with steam and sulfuric acid (H_2SO_4) catalyst

Test for unsaturation

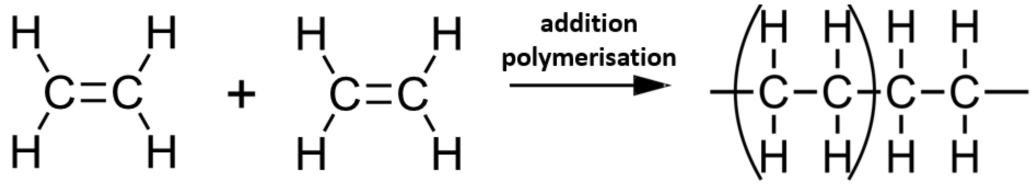
- Saturated molecules have carbon to carbon single bonds.
- Unsaturated molecules have carbon to carbon double or triple bonds (multiple bonds).
- Bromine water, $Br_{2(aq)}$, can be used to distinguish between an alkane and an alkene.
- Bromine water is a brown-coloured solution.
- When added to an alkene, the bromine water is delcolourised (brown to colourless).
- This indicates the presence of carbon to carbon double bonds in the molecule.
- When added to an alkane, there is no colour change.

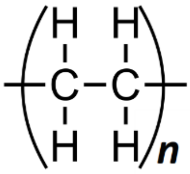
Concept check: Outline the test for unsaturation.

React with bromine water, Br_2(aq). The bromine water will be decolorised in the alkene (colour change brown to colourless) but there will be no colour change with an alkane (bromine water will stay brown).

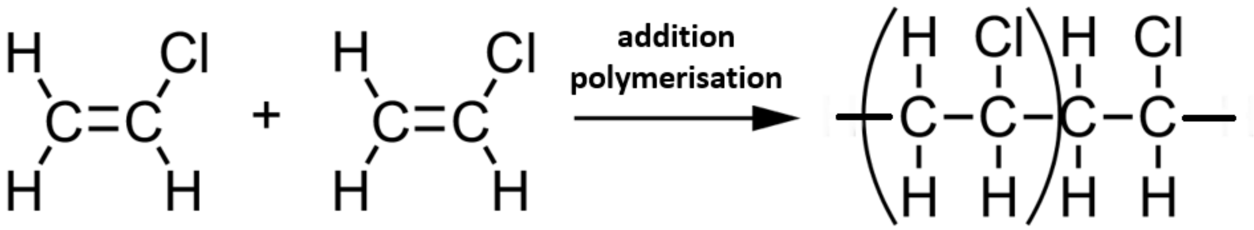
Addition polymerisation

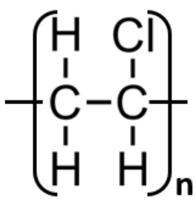
- Addition polymers are formed when smaller unsaturated molecules (monomers) react together.
- Poly(ethene) is formed when ethene monomers react together to form



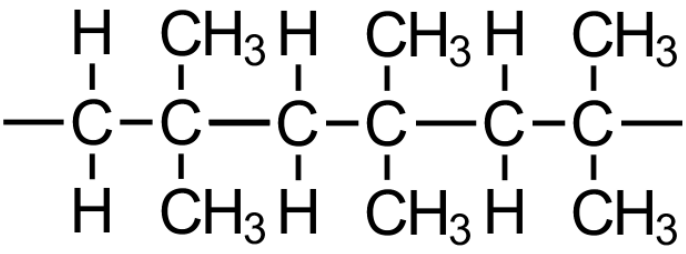


- PVC or poly(vinyl chloride) is a polymer made from the monomer unit chloroethene (vinyl chloride).



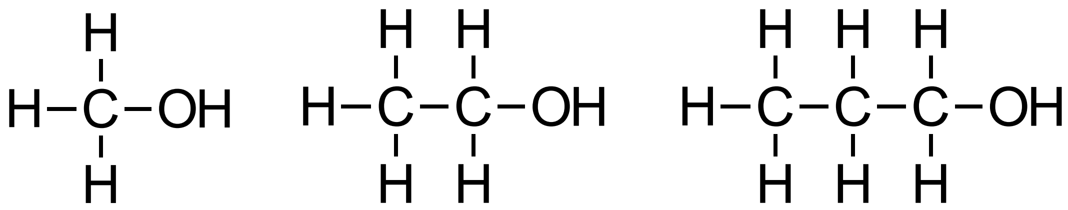


Concept check: Draw the structure of the polymer made from three 2-methylpropene monomer units.



Reactions of the alcohols

- Alcohols are organic compounds composed of carbon, hydrogen and oxygen.
- Alcohols undergo combustion and oxidation reactions.



Combustion reactions of the alcohols

- Alcohols undergo combustion in excess oxygen (complete combustion) to form carbon dioxide and water.

$$2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$

$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

Oxidation reactions of the alcohols

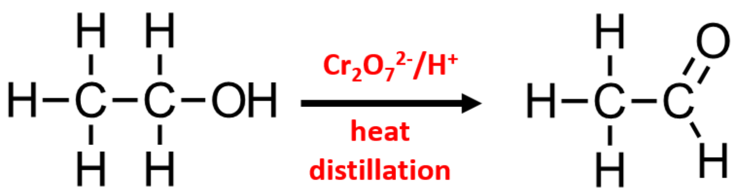
- Alcohols undergo oxidation reactions when reacted with a suitable oxidising agent such as acidified potassium dichromate(VI), $H^+/Cr_2O_7^{2-}$.
- Colour change is orange to green ($Cr_2O_7^{2-}$ ion is reduced to the Cr^{3+} ion).

$$\mathbf{Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightarrow 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)}}$$

- An alternative oxidising agent is acidified potassium manganate(VII) solution which changes colour from purple to colourless as the manganate(VII) ion, MnO_4^-, is reduced to the manganese(II) ion, Mn^{2+}.

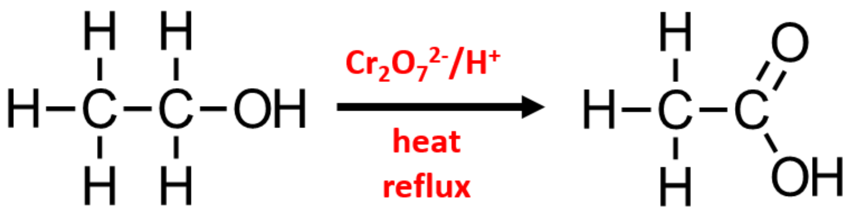
$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \rightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

- Primary alcohols undergo partial oxidation to form aldehydes.



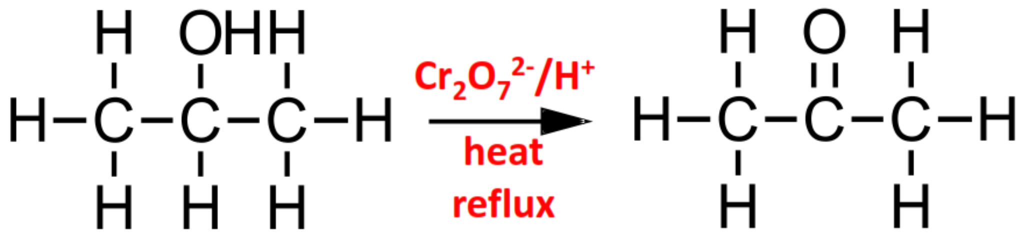
- An excess of alcohol is used in the reaction and the aldehyde is distilled off as it is produced.

- Primary alcohols can also undergo complete oxidation to form carboxylic acids.



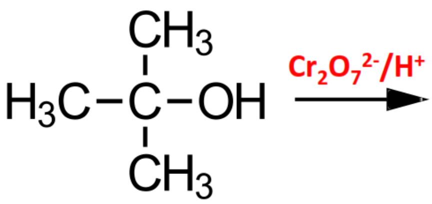
- An excess of oxidising agent is used in the reaction.

- Secondary alcohols are oxidised by acidified potassium dichromate(VI) ($Cr_2O_7^{2-}/H^+$) and heat to form ketones.



- Colour change is orange to green ($Cr_2O_7^{2-}$ ion is reduced to the Cr^{3+} ion).

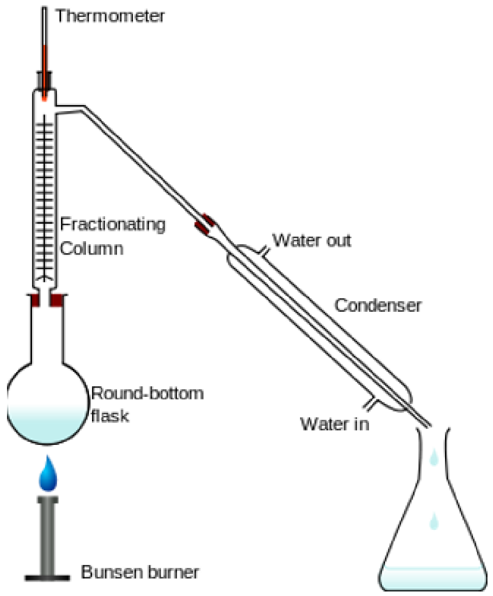
- Tertiary alcohols cannot be oxidized by acidified potassium dichromate(VI) ($Cr_2O_7^{2-}/H^+$) (no H atoms bonded directly to C-OH).



No reaction (no colour change).

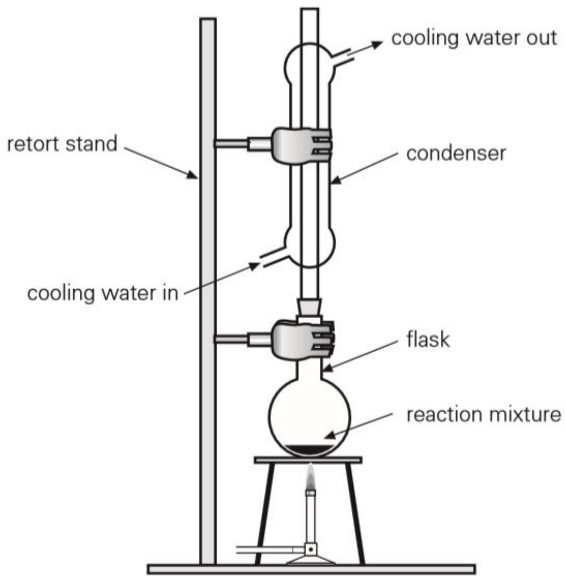
Distillation

- Distillation is used to separate the components of a mixture that have different boiling points.
- Aldehydes, due to their weaker intermolecular forces, have lower boiling points than alcohols.
- The aldehyde evaporates, rises up the fractionating column and condenses to form a liquid.



Reflux

- A reflux condenser is used to prevent the loss of a solvent from a mixture.
- The vapours rise up the column, condense, and flow back down to the flask.
- The reaction mixture and oxidising agent are kept in contact for a longer period of time.



Exercises:

1) Write equations for the complete combustion of the following:

a) $2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)}$

b) $2C_3H_7OH_{(l)} + 9O_{2(g)} \rightarrow 6CO_{2(g)} + 8H_2O_{(l)}$

c) $C_4H_9OH_{(l)} + 6O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)}$

2) Propan-1-ol and propan-2-ol are two structural isomers of C_3H_8O.
Both propan-1-ol and propan-2-ol can be oxidized in aqueous solution.

(i) State any necessary conditions for the oxidation to occur and describe the colour change during the oxidation process.

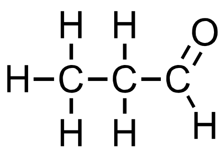
Heat with distillation or reflux

Oxidizing agent is acidified potassium dichromate(VI) or potassium manganate(VII)

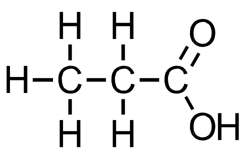
Colour change is orange to green

(ii) When propan-1-ol is oxidized using a warm acidified solution of potassium dichromate(VI) two different organic products can be obtained. Deduce the name and structural formula for each of these two products.

propanal CH_3CH_2CHO

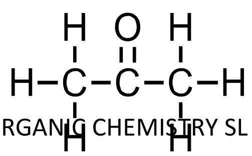


propanoic acid CH_3CH_2COOH



(iii) Identify the class of alcohols that propan-2-ol belongs to and state the name of the organic product formed when it is oxidized by an acidified solution of potassium dichromate(VI).

(iii)

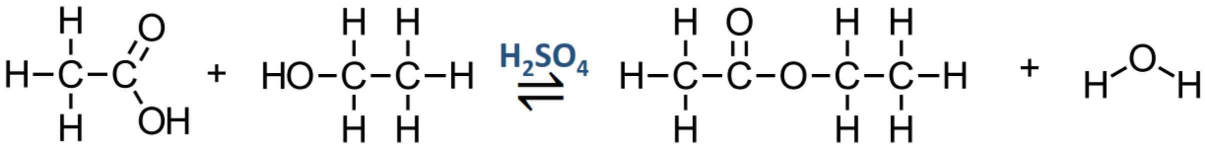


propan-2-ol is a secondary alcohol
oxidizes to propanone

Esters

- Alcohols and carboxylic acids react to form esters.
- This is a nucleophilic substitution reaction (it is also called a condensation or esterification reaction).
- The catalyst is concentrated sulfuric acid (conc. H_2SO_4).

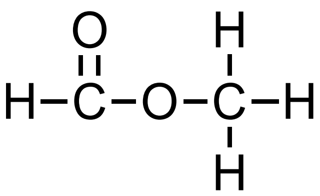
carboxylic acid + alcohol ⇌ ester + water



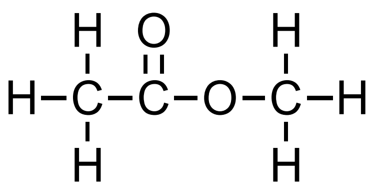
$$CH_3COOH_{(l)} + CH_3CH_2OH_{(l)} \rightleftharpoons CH_3COOCH_2CH_{3(l)} + H_2O_{(l)}$$

- Esters have distinctive fruity smells.
- Esters are used as natural and artificial food flavorings.
- They are also used as solvents in perfumes and as plasticizers.

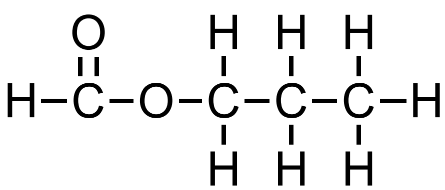
Naming esters



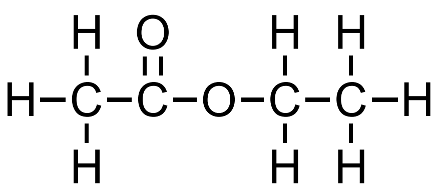
Methyl methanoate



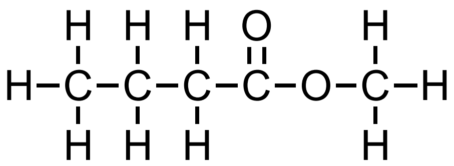
Methyl ethanoate



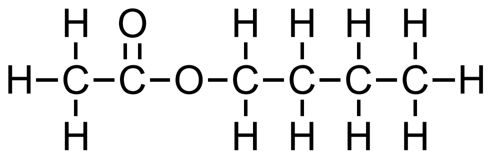
Propyl methanoate



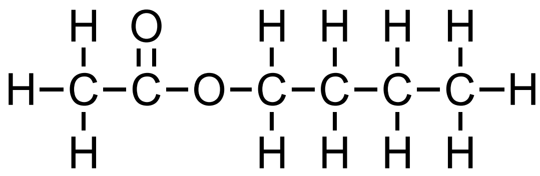
Ethyl ethanoate



Methyl butanoate



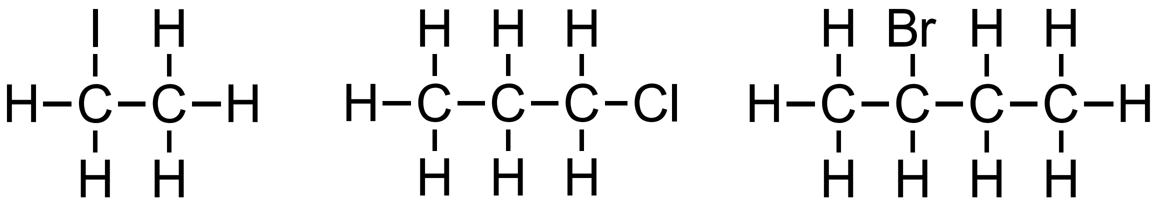
Butyl ethanoate



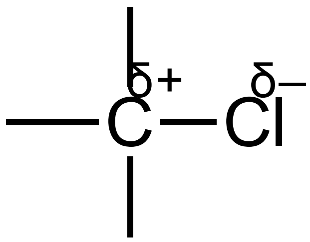
Butyl ethanoate

Reactions of halogenoalkanes

- General formula $C_nH_{2n+1}X$
- Halogenoalkanes contain an atom of fluorine, chlorine, bromine or iodine.

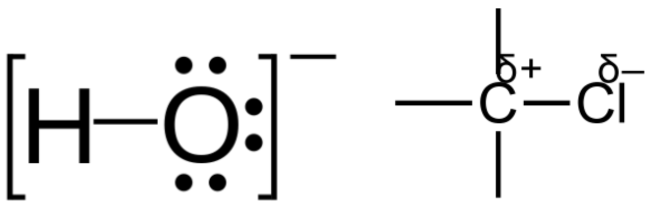


- Halogenoalkanes undergo substitution nucleophilic reactions (the replacement of one atom by another atom or group).

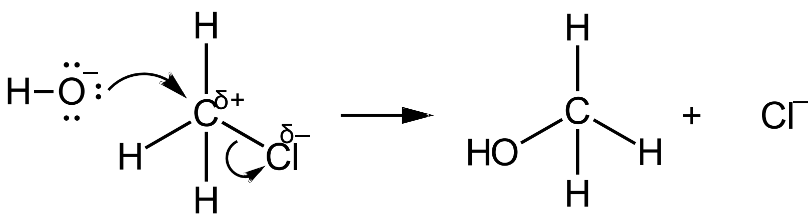


The halogen is more electronegative than the carbon atom forming a polar bond.
The halogen has a partial negative charge and the carbon has a partial positive charge (electron deficient).

- Nucleophiles are electron rich species that contain a lone pair of electrons that it donates to an electron deficient carbon.



- The hydroxide ion (nucleophile) is attracted to the electron deficient carbon in the halogenoalkane.



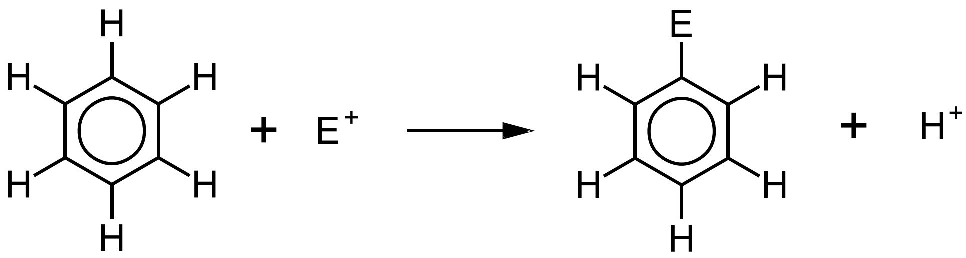
$$CH_3Cl_{(g)} + NaOH_{(aq)} \rightarrow CH_3OH_{(l)} + NaCl_{(aq)}$$

- The C-Cl bond breaks heterolytically (heterolytic bond fission).
- The conditions are warm with aqueous NaOH.

Reactions of benzene

The delocalized π electrons give benzene extra stability, therefore it does not undergo addition reactions.

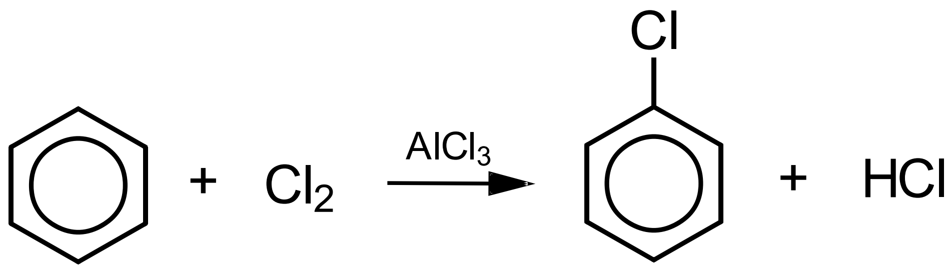
- Benzene undergoes electrophilic substitution reactions in which a hydrogen atom is replaced by an incoming group.



- An electrophile is a reactant which is electron deficient (has a partial positive charge).
- The electrophile is attracted to the electron rich benzene ring.

Reaction with chlorine (Cl_2)

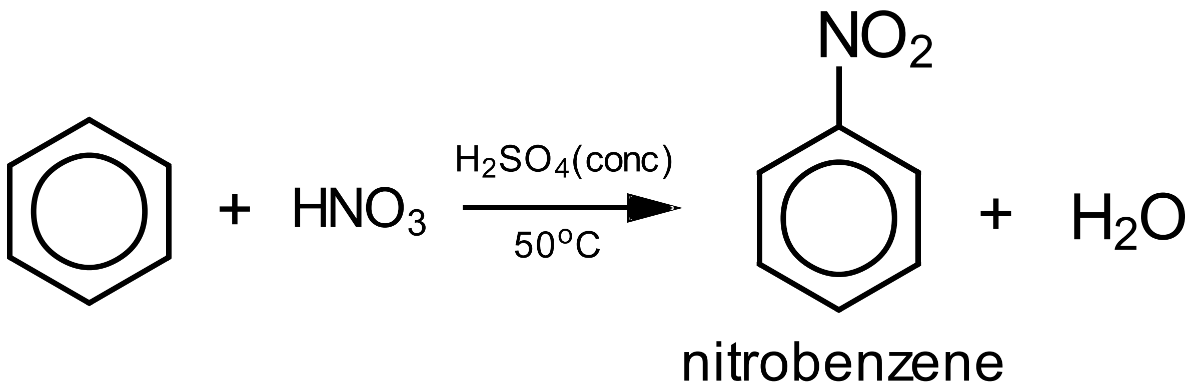
- Benzene reacts with chlorine to form chlorobenzene.



$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

Reaction with nitric acid (HNO_3)

- Benzene reacts with nitric acid to form nitrobenzene.



$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$