H2 Chemistry Organic Booklet 1

Contents

References

1. Chemistry for Advanced Level by P. Cann & P. Hughes, published by John Murray
2. A-Level Chemistry (4th Edition) by E. N. Ramsden, published by Nelson Thornes
3. Understanding Chemistry for Advanced Level (3rd Edition), by T. Lister & J. Renshaw, published by Nelson Thornes
4. Chemistry in Context (5th Edition) by Hill & Holman, published by Nelson Thornes
5. Chemistry in Context Laboratory Manual and Study Guide (5th Edition) by Hill & Holman, published by Nelson Thornes
6. ILPAC Advanced Practical Chemistry (2nd edition) by A. Lainchbury, J. Stephens, A. Thompson, published by John Murray
7. A2 Chemistry, 2nd edition, Geroge Facer
8. Longman A-level course in Chemistry, 7th edition, JGR Briggs
9. Organic Chemistry, 5th edition, John McMurry

Organic Chemistry
Preamble

Although there are features of organic chemistry topics that are distinctive, it is intended that appropriate cross-references with other sections/topics in the syllabus should be made.

In their study of organic chemistry, candidates may wish to group the organic reactions in terms of the mechanisms in the syllabus where possible. Candidates may wish to compare and contrast the different mechanisms.

When describing preparative reactions, candidates will be expected to quote the reagents, e.g. aqueous NaOH, the essential practical conditions, e.g. reflux, high temperature and pressure, and the identity of each of the major products. Detailed conditions involving specific temperature and pressure values are **not** required.

Detailed knowledge of practical procedures is also **not** required; however, candidates may be expected to suggest (from their knowledge of the reagents, essential conditions and products) what steps may be needed to purify/extract a required product from the reaction mixture. In equations for organic redox reactions, the symbols [O] and [H] are acceptable.

11.1 Introduction

Content

- Empirical, molecular and structural formulae
- Functional groups and the naming of organic compounds
- Common terms for organic reactions and reactivities
- Shapes of organic molecules; σ and π bonds

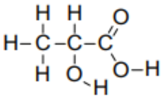
Candidates are expected to be able to interpret and use the following types of representations in the description of organic molecules. The examples given are for the compound (+)-lactic acid.

Empirical Formula: simplest ratio of the number of atoms of the elements present in one molecule, e.g. CH_2O

Molecular Formula: actual number of atoms of the elements present in one molecule, e.g. $C_3H_6O_3$

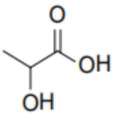
Structural Formula: shows how the constituent atoms of a molecule are joined together with minimal detail, using conventional groups, for an unambiguous structure, e.g. $CH_3CH(OH)CO_2H$

Full Structural or Displayed Formula: detailed structure of molecule showing the relative placing of atoms and the number of bonds between them, e.g.

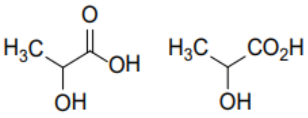


Skeletal Formula: simplified representation of an organic formula derived from the structural formula by removing hydrogen atoms (and their associated bonds) and carbon atoms from alkyl chains, leaving just the carbon-carbon bonds in the carbon skeleton and the associated functional groups

Skeletal or partial skeletal representations may be used in question papers and are acceptable in candidates' answers where they are unambiguous, e.g.



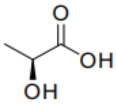
skeletal



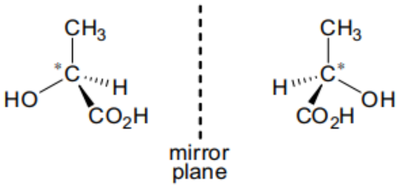
partial skeletal

The convention  for representing the aromatic ring is preferred.

Stereochemical Formula: show spatial arrangement of bonds, atoms and groups in molecule in 3-D, e.g.

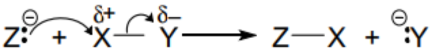


When drawing a pair of optical isomers, candidates should indicate the three-dimensional structures according to the convention used in the example below.

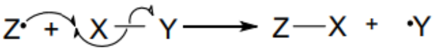


Candidates are expected to be able to interpret and use the curly arrow notation to represent the movement of electrons in organic reaction mechanisms.

For movement of a *pair* of electrons (**full arrow**) :



For movement of a *single* unpaired electron (**half arrow**) :



Learning Outcomes

Candidates should be able to:

(a) interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound:
  (i) hydrocarbons (alkanes, alkenes and arenes)
  (ii) halogen derivatives (halogenoalkanes and halogenoarenes)
  (iii) hydroxyl compounds (alcohols and phenols)
  (iv) carbonyl compounds (aldehydes and ketones)
  (v) carboxylic acids and derivatives (acyl chlorides and esters)
  (vi) nitrogen compounds (amines, amides, amino acids and nitriles)

(b) interpret, and use the following terminology associated with organic reactions:
  (i) functional group
  (ii) degree of substitution: primary, secondary, tertiary, quaternary
  (iii) homolytic and heterolytic fission
  (iv) carbocation
  (v) free radical, initiation, propagation, termination
  (vi) electrophile (Lewis acid), nucleophile (Lewis base)
  (vii) addition, substitution, elimination, condensation, hydrolysis
  (viii) oxidation and reduction

  [in equations for organic redox reactions, the symbols [O] and [H] are acceptable]

(c) interpret, and use the following terminology associated with organic reactivities:
  (i) delocalisation
  (ii) electronic effect (electron-donating and electron-withdrawing effect)
  (iii) steric effect (steric hindrance)

(d) describe sp^3 hybridisation, as in ethane molecule, sp^2 hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule

(e) explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to σ and π carbon-carbon bonds

(f) predict the shapes of, and bond angles in, molecules analogous to those specified in (e)

(g) apply (b) and (c) to the understanding of mechanisms in terms of organic structure and bonding

(h) recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites

11.2 Isomerism

Content

- Isomerism: *constitutional (structural); cis-trans; enantiomerism*

Learning Outcomes

Candidates should be able to:

(a) describe constitutional (structural) isomerism

(b) describe *cis-trans* isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds

[use of *E*, *Z* nomenclature is **not** required]

(c) explain what is meant by a chiral centre

(d) deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry

(e) recognise that an optically active sample rotates plane-polarised light and contains chiral molecules

(f) recognise that enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light

[usage of the term diastereomers is **not** required]

(g) recognise that enantiomers have identical chemical properties except in their interactions with another chiral molecule

(h) recognise that different stereoisomers exhibit different biological properties, for example in drug action

(i) deduce the possible isomers for an organic molecule of known molecular formula

(j) identify chiral centres and/or *cis-trans* isomerism in a molecule of given structural formula

In each of the sections below, 11.3 to 11.8, candidates will be expected to be able to predict the reaction products of a given compound in reactions that are chemically similar to those specified.

11.3 Hydrocarbons

Content

- Alkanes (exemplified by ethane)
  - (i) free-radical substitution reactions
- Alkenes (exemplified by ethene)
  - (i) electrophilic addition, including Markovnikov's rule
  - (ii) reduction and oxidation reactions
- Arenes (exemplified by benzene and methylbenzene)
  - (i) influence of delocalised π electrons on structure and properties
  - (ii) electrophilic substitution reactions
  - (iii) oxidation of side-chain
- Hydrocarbons as fuels

Learning Outcomes

Candidates should be able to:

(a) explain the general unreactivity of alkanes, including towards polar reagents

(b) describe the chemistry of alkanes as exemplified by the following reactions of ethane:
   (i) combustion
   (ii) free-radical substitution by chlorine and by bromine

(c) describe the mechanism of free-radical substitution with particular reference to the initiation, propagation and termination reactions

(d) explain the general reactivity of alkenes towards electrophilic reagents/electrophiles

(e) describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene:
   (i) electrophilic addition of water/steam, hydrogen halides and halogens
   (ii) reduction via catalytic hydrogenation (catalytic addition of hydrogen; see also 8(j))
   (iii) oxidation by cold, alkaline solution of manganate(VII) ions to form the diol
   (iv) oxidation by hot, acidified solution of manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules

(f) describe the mechanism of electrophilic addition in alkenes, using bromine with ethene as an example

(g) apply Markovnikov's rule to the addition of hydrogen halides to unsymmetrical alkenes, and explain the composition of products in terms of the stability of carbocation intermediates

(h) explain, in terms of delocalisation of π electrons, the difference between benzene and alkene:
   (i) reactivity towards electrophiles
   (ii) preference of benzene to undergo substitution rather than addition reaction

(i) describe the chemistry of the benzene ring as exemplified by the following reactions of benzene and methylbenzene:
   (i) electrophilic substitution reactions with chlorine and with bromine
   (recognise the use of Lewis acid as catalysts; see also Section 4)
   (ii) nitration with concentrated nitric acid
   (recognise concentrated sulfuric acid as a Brønsted-Lowry acid catalyst; see also Section 4)
   (iii) Friedel-Crafts alkylation with halogenoalkanes
   (recognise the use of Lewis acid as catalysts; see also Section 4)

(j) (i) describe the mechanism of electrophilic substitution in arenes, using the mono-bromination of benzene as an example
   (ii) describe the effect of the delocalisation of electrons in arenes in such reactions

(k) describe the chemistry of the alkyl side-chain of benzene ring as exemplified by the following reactions of methylbenzene:
   (i) free-radical substitution by chlorine and by bromine
   (ii) complete oxidation to give benzoic acid

(l) predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions

(m) apply the knowledge of positions of substitution in the electrophilic substitution reactions of mono-substituted arenes

(n) recognise the environmental consequences of:
   (i) carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal
   (ii) gases that contribute to the enhanced greenhouse effect

(o) recognise that petroleum, a chemical feedstock, is a finite resource and the importance of recycling

1 INTRODUCTION TO ORGANIC CHEMISTRY

1.1 THE ORIGINS OF ORGANIC CHEMISTRY

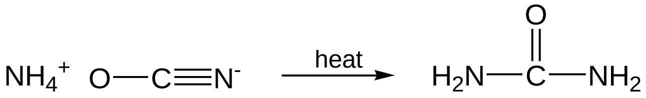
The modern definition of *organic chemistry* is the study of compounds that contain carbon.

Jon Jacob Berzelius

Originally, the science of organic chemistry was the study of compounds extracted from living organisms and their natural products. In 1807, Jon Jacob Berzelius classified chemical compounds into two main groups: those with origin from living or once-living matter, which he termed **organic** and those that originated from "mineral" or non-living matter, which he termed **inorganic**. Berzelius, similar to most chemists of that era, believed that organic compounds could only come from living organisms mediated by some vital force, known as **Vitalism**.]

Frederich Wöhler

In 1828, Frederich Wöhler, ironically a student of Berzelius, discovered that the organic compound, urea, could be made by heating ammonium cyanate, an inorganic salt. This demonstrated for the very first time that an organic compound can be synthesised from an inorganic source, which led eventually to the rejection of Vitalism as a scientific theory.



$$NH_4^+\ O-C\equiv N^- \xrightarrow{\text{heat}} H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

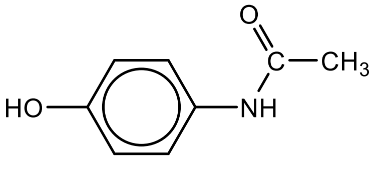
ammonium cynate urea

Wöhler's observation also marked the discovery of **isomerism** – the phenomenon of two or more different chemical structures based on the same chemical formula.

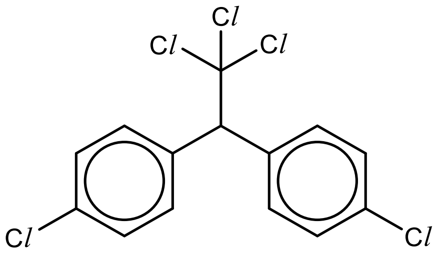
Today, chemistry is unified and the same principles that explain inorganic compounds explain the organic ones as well. The only distinguishing characteristic of organic compounds is that all contain the element **carbon**.

Organic chemistry is the chemistry of carbon and its compounds, which are central to life. Carbon is present in all large and complex molecules in all living species. The diversity of life is a manifestation of the diversity of carbon chemistry. The ability of carbon to form a virtually unlimited range of compounds has led to an almost unlimited range of living organisms constructed out of molecules containing carbon.

More than 10 million compounds we encounter in our daily lives are organic compounds. They are found in fuels, plastics, synthetics and natural fibers such as polyester, dyes, cottons, drugs, pesticides, preservatives, flavorings, etc.



Paracetamol
(Panadol)



Dichlorodiphenyltrichloroethane (DDT)
(Insecticide)

1.2 REASONS FOR THE VAST VARIETY OF ORGANIC COMPOUNDS

Carbon has 3 important properties that enable it to form many stable compounds.

(i) Ability of carbon to form strong C–C bonds

Bond	Bond energy / kJ mol^{-1}
C–C	350
C–O	360
C–C*l*	340
C–H	410

The C–C bond is strong and its strength is comparable to that of the C–O and C–C*l* bonds. This **ability of carbon to form strong bonds with itself leads to the formation of chains and rings of different lengths / sizes**.

(ii) Ability of carbon to form multiple bonds

A carbon atom has 4 valence electrons, hence can form covalent bonds with as many as 4 other atoms. This gives rise to branching into side chain of other carbon atoms

Carbon can also undergo different types of **hybridisation** (**sp, sp^2 and sp^3**) resulting in the formation of single, double and triple bonds between carbon atoms and between carbon and other atoms, leading to a greater variety of stable compounds of different structure/shapes.

(iii) Kinetic stability of carbon compounds under normal conditions

Methane and most other carbon-containing compounds are **thermodynamically less stable** than their combustion products. However, they are **kinetically stable** as they **react only very slowly**, if at all, with oxygen under normal conditions.

This is mainly due to:

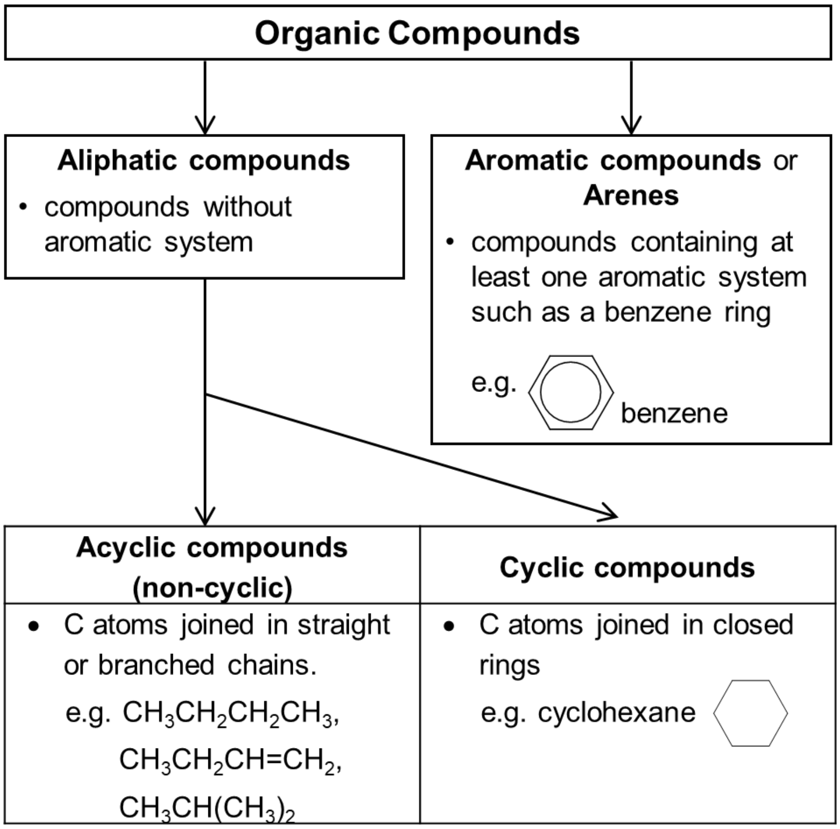
- strong C–C and C–H bonds. This breaking of C–C requires relatively large energy of activation.
- inability of C to expand its octet.

1.3 INTRODUCTION TO ORGANIC COMPOUNDS

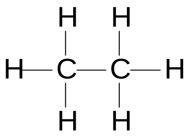
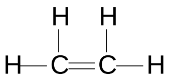
Success Criteria:

- I can classify organic compounds into aliphatic, aromatic, acyclic and cyclic compounds.
- I can explain and recognise what saturated and unsaturated organic compounds are.

1.3.1 Classifications of Organic Compounds



Saturated and unsaturated organic compounds

An organic compound which contains only single bonds (C–C and C–H bonds in hydrocarbons) is said to be **saturated.** 	An organic compound which contains 1 or more double / triple bonds (C=C, C=O and C≡N bonds) is said to be **unsaturated**. 

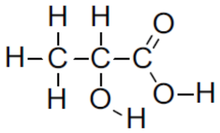
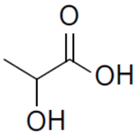
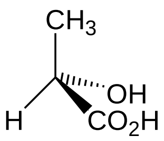
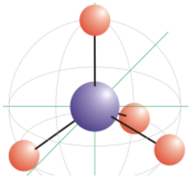
1.3.2 Structural Formulae of Organic Compounds

Success Criteria:
- I can interpret and draw different types of structural formulae (eg condensed, displayed, skeletal and stereochemical).

Lactic acid has a molecular formula of $C_3H_6O_3$ and an empirical formula of CH_2O.

A molecular formula does not show how the various atoms in the organic compound are actually connected to one another. Hence, structural formulae are used to represent organic compounds.

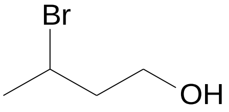
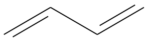
Below are the different structural formulae of lactic acid, $CH_3CH(OH)CO_2H$.

Type of Structural Formulae	Representation	Characteristics
Condensed	$CH_3CH(OH)CO_2H$	• shows the order of arrangement of atoms • bonds are not displayed
Displayed / Full structural		• shows **all** atoms and bonds in the molecule
Skeletal		• Carbon atoms in a straight chain are drawn in a zigzag manner • each end of a line represents a carbon if other symbol of an atom is **not** written • C–H bonds at each C are **not** shown. • each C forms 4 bonds. Any “missing” bond not drawn out in a skeletal structure would be a C–H bond.
Stereochemical (for optical isomers where a C has four different groups attached)	 or	• shows 3-D spatial arrangement of bonds, atoms and / or groups of atoms in a molecule • a dashed line (┈┈┈) represents a bond **<u>into</u>** the plane of the paper • a wedged line (▶) represents a bond **<u>out</u>** of the plane of the paper 

Video on Drawing Skeletal Formula.

https://tinyurl.com/skeletalformula

More examples of skeletal structures.

Condensed formula	$CH_3CH(Br)CH_2CH_2OH$	$CH_2{=}CHCH{=}CH_2$
Skeletal formula		

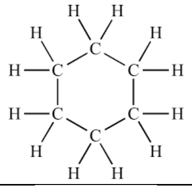
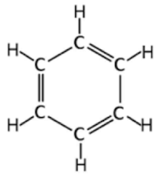
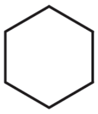
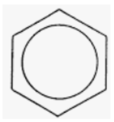
Checkpoint 1

Complete the following table.

Type of formula	**Compound**	**Compound**
Condensed	$HOCH_2CH_2OH$	$CH_3CH{=}CH_2$
Displayed / full structural		
Skeletal		

1.3.3 Representation of carbon rings in formulae

Cyclic rings of atoms are often represented by their skeletal formula.

Name	Cyclohexane	Benzene
Molecular Formula	C_6H_{12}	C_6H_6
Structural Formula		
Skeletal Formula		

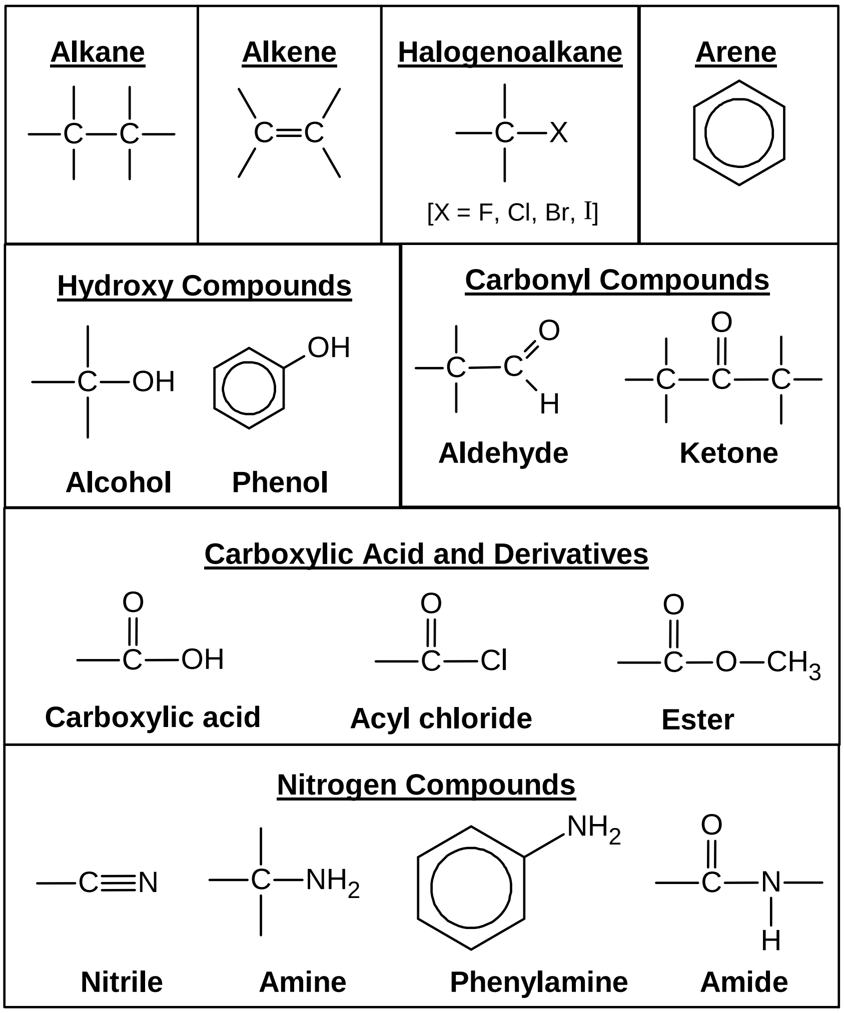
1.3.4 Functional groups

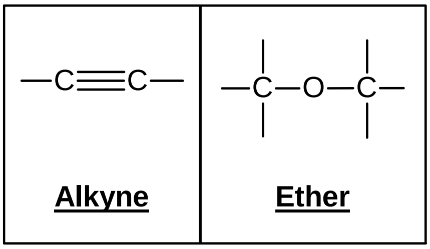
Success Criteria:
- I can identify, name and draw the functional groups

Video on
Functional Groups
Memorizing Tricks

https://tinyurl.com/functionalgroup

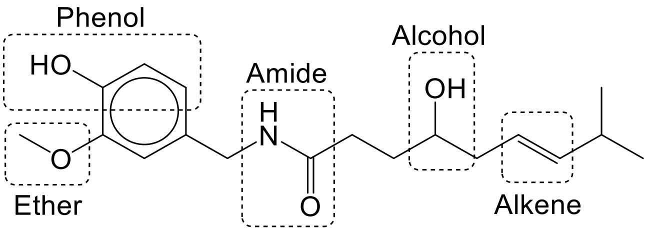
A **functional group** is made up of an atom (e.g. C*l*) or a group of atoms (e.g. –OH, –CN) responsible for the characteristic chemical properties of an organic compound.





These 2 functional groups are not in H2 syllabus.

Capsaicin, an active component of chili peppers responsible for the burning sensation, contains several functional groups. Are you able to identify them?



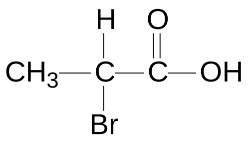
1.3.5 Nomenclature of Organic Compounds

Success Criteria:
- I can name the organic compound using IUPAC system and construct the structural formula of a compound from its IUPAC name.

Naming of organic compounds is based on a systematic method developed by the **I**nternational **U**nion of **P**ure and **A**pplied **C**hemists (IUPAC).

Every IUPAC name consists of a **parent** (or **stem**), a **suffix** and as many **prefixes** as necessary.

Prefix(es)	Parent	Suffix
Substituents	Longest continuous carbon chain bearing the principal (most important) functional group	Principal functional group



$CH_3-CH(Br)-COOH$

2-bromopropanoic acid

(a) Parent

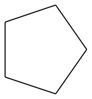
In the aliphatic unbranched chain system, the name of the parent takes its name according to the number of carbon atoms in the longest continuous chain.

no. of carbon	*parent*
1	**meth-**
2	**eth-**
3	**prop-**
4	**but-**
5	**pent-**

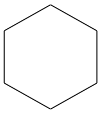
no. of carbon	*parent*
6	**hex-**
7	**hept-**
8	**oct-**
9	**non-**
10	**dec-**

For **saturated** hydrocarbon, the name of the parent ends with **-an-**. For an unsaturated hydrocarbon with C=C bond, the name of the parent ends with -en-.

In **cyclic** molecules, the word **cyclo** is added to the left of the parent (or stem) of their IUPAC name.



cyclopentane



cyclohexane

(b) Suffix

- It indicates the **principal functional group** of the organic compound.
- *Table 1* gives the list of the functional groups in decreasing order of priority as suffix. The functional group(s) other than principal functional groups are as prefix(es).

decreasing priority

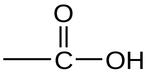
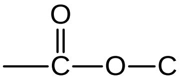
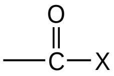
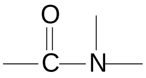
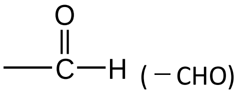
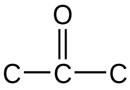
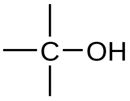
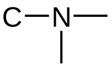
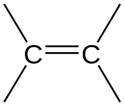
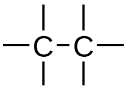
Functional group	*Type of compound*	*Suffix*
 $-\overset{O}{\overset{\|}{C}}-OH$	**carboxylic acid**	**-oic acid**
 $-\overset{O}{\overset{\|}{C}}-O-C$	**ester**	**(alk)yl …-oate**
 $-\overset{O}{\overset{\|}{C}}-X$	**acyl halide**	**-oyl halide**
 $-\overset{O}{\overset{\|}{C}}-\underset{}{\overset{\|}{N}}-$	**amide**	**-amide**
$-C\equiv N$	**nitrile**	**-nitrile**
 $-\overset{O}{\overset{\|}{C}}-H$ (− CHO)	**aldehyde**	**-al**
 $C-\overset{O}{\overset{\|}{C}}-C$	**ketone**	**-one**
 $-\underset{\|}{\overset{\|}{C}}-OH$	**alcohol**	**-ol**
 $C-\underset{\|}{N}-$	**amine**	**-amine**
	**alkene**	**-ene**
 $-\underset{\|}{\overset{\|}{C}}-\underset{\|}{\overset{\|}{C}}-$	**alkane**	**-ane**

Table 1. Suffixes of various functional groups

(c) Prefix

- Once the principal functional group is identified, any other functional group in the compound is treated as a substituent on the parent chain, and is named by a prefix.
- A **substituent group** is an atom or group of atoms substituted in place of a hydrogen atom on the parent chain of a hydrocarbon.

Substituent group	*Prefix*
–F	fluoro-
–C*l*	chloro-
–Br	bromo-
–I	iodo-
–OH	hydroxy-
$–NO_2$	nitro-
–CN	cyano-
$–NH_2$	amino-

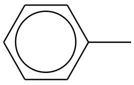
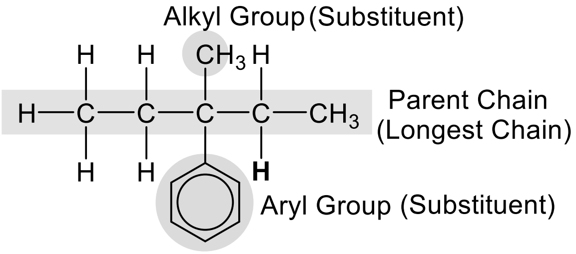
Substituent group	*Prefix*
Alkyl group	
CH_3–	methyl-
CH_3CH_2–	ethyl-
$CH_3CH_2CH_2$–	propyl-
Aryl group  or C_6H_5–	phenyl-

Table 2. Common prefixes

Arabic numerals (1,2,3) are used to indicate the **positions of attachment** of substituents, C=C bonds and certain principal functional groups. They are known as **positional numbers**.

3-methyl-3-phenylpentane

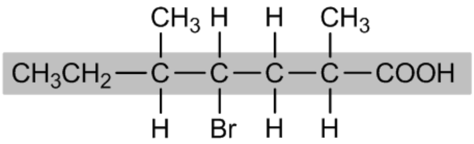
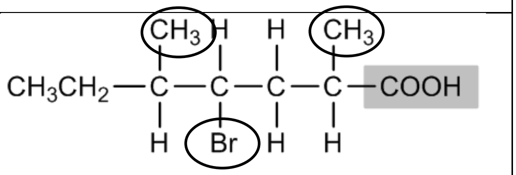
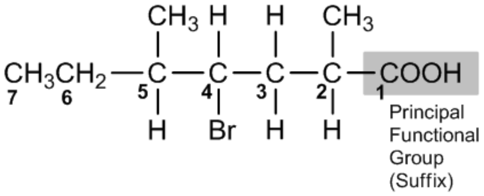
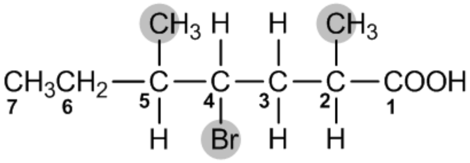


For carbon chain with 3 carbon or more, we need to specify the position of the principal functional group. The position of the double bond is denoted using the smaller carbon number.

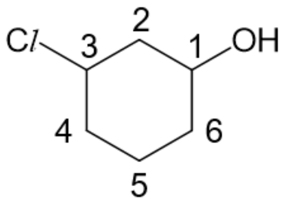
E.g. But-2-ene shows that the C=C is between C2 and C3

$CH_3CH_2CH=CH_2$	$CH_3CH=CHCH_3$
But-1-ene	But-2-ene

Key Steps in naming organic compounds

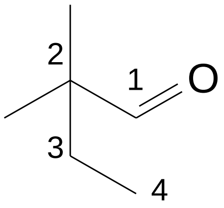
	Steps	*Example*
1	Identify the longest continuous carbon chain containing the principal functional group (functional group with the highest priority). Count the number of C atoms. This gives the **parent**.	 $CH_3CH_2-C(CH_3)(H)-C(H)(Br)-C(H)(H)-C(CH_3)(H)-COOH$ ● no. of C atoms in parent chain = 7 **parent**: **hept-**
2	Identify all the functional groups and write the principal functional group as the suffix and the rest as the prefixes.	 $CH_3CH_2-C(CH_3)(H)-C(H)(Br)-C(H)(H)-C(CH_3)(H)-COOH$ ● carboxylic acid functional group is of the highest priority **suffix**: **-anoic acid** **Prefixes:** "bromo-" and "methyl-"
3	Number C atoms in the longest chain (from one end) such that: i) the **principal functional** group will be assigned the lowest possible number. ii) and then the **lowest** individual numbers for the substituents.	 $CH_3CH_2-C(CH_3)(H)-C(H)(Br)-C(H)(H)-C(CH_3)(H)-COOH$
4	String together the prefix(es), parent, and suffix taking note of the following rules. ● If the same substituent appears more than once, use *di-(two), tri-(three), tetra-*(four), etc. The appropriate positional number is still required even if the groups are connected to the same carbon on the parent chain. ● Different prefixes are listed in alphabetical order; multiple prefixes like *di-* and *tri-* do not affect the alphabetical order. Commas (,) are used to separate numbers and hyphens (-) to separate numbers and alphabets.	 $CH_3CH_2-C(CH_3)(H)-C(H)(Br)-C(H)(H)-C(CH_3)(H)-COOH$ **Prefixes:** "bromo-" and 2 × "methyl-" **Position of** "bromo-": carbon 4 **Positions of** "methyl-": on carbon 2 and 5 **Parent**: heptanoic acid The name of the compound is **4-bromo-2,5-dimethylheptanoic acid.**

Worked Example 1



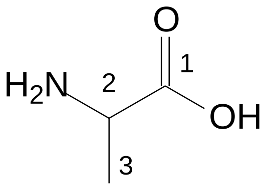
parent: cyclohex
suffix: -ol
prefix: chloro on carbon 3

The name is 3-chlorocyclohexanol



parent: but
suffix: -al
prefix: 2 × methyl on carbon 2 and 2

The name is 2,2-dimethylbutanal



parent: prop
suffix: -oic acid
prefix: amino on carbon 2

The name is 2-aminopropanoic acid

1.3.6 Homologous Series

A **homologous series** is a family of organic compounds having the same **functional group**; **each successive member increases by a –CH_2– unit**.

Compounds in the same homologous series:

- can be represented by a general molecular formula (e.g. alkane, C_nH_{2n+2}).
- show a gradual change in physical properties (density, melting and boiling points, solubility, etc.) with an increase in molar mass.
- have similar chemical properties as they have the same functional group(s).
- can usually be prepared by similar methods.

Homologous series of alkanes

Formula	*Name*	*Boiling point / ºC*
CH_4	methane	–162
CH_3CH_3	ethane	–89
$CH_3CH_2CH_3$	propane	–42

Note:
For carbon chain with 3 carbon or more, we need to specify the position of the principal functional group.

Homologous series of alkene

Formula	*Name*
$CH_2=CH_2$	Ethene
$CH_3CH=CH_2$	Propene
$CH_3CH_2CH=CH_2$	But-1-ene
$CH_3CH=CHCH_3$	But-2-ene

Homologous series of alcohol

Formula	*Name*
CH_3OH	Methanol
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2OH$	Propan-1-ol
$CH_3CH(OH)CH_3$	Propan-2-ol

Note:
If no position is assigned for principal functional group, we can assume that it is located at the 1st carbon in the longest chain.

Checkpoint 2

1. Draw the structure of the following compounds.

IUPAC name	compound
pentan-3-one	
2-hydroxy-4-methylhexanal	
3-bromo-1-methylcyclopentene	

1.4 CHEMICAL BONDING FOR ORGANIC CHEMISTRY

1.4.1 Hybridisation and Hybrid Orbitals

Success Criteria:

- I can identify type of hybridisation a central atom undergoes by looking at its electron geometry.
- I can show, through the use of orbital diagrams (both hybrid and unhybridised), how the sigma bond and pi bonds are formed with the carbon centre.

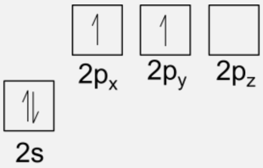
- Hybridisation is a model used to explain the **observed shapes** of molecules about the central atom**.**

- Hybridisation model shows **mixing of pure atomic orbitals** in an atom to generate **a set of degenerate hybrid orbitals (hybrid orbitals are of same energy level)**.

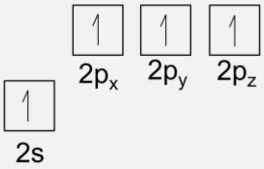
Why is hybridisation proposed? (For information ONLY)

Let's consider a methane molecule, CH_4. The shape about C is tetrahedral with a bond angle of 109.5°.

The valence shell electronic configuration of C is: $2s^2\ 2p^2$ at different energy levels as shown below.

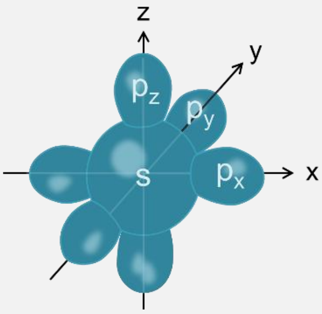


When C forms 4 covalent bonds with 4 H atoms as in CH_4, all its 4 valence electrons are used. The electrons must be unpaired before each can pair with another electron from H to form a covalent bond. Thus, an electron in the valence shell needs to be excited or promoted from the 2s to 2p orbitals so as to get 4 unpaired electrons in the excited state,



no. of unpaired electrons
= no. of bonds formed

This would then result in an arrangement of atomic orbitals as shown below where the spherical s orbital and dump-bell shaped p orbitals are arranged at 90° to each other.



2s and 2p
atomic orbitals of C

If this were true:

- each CH_4 molecule will have a bond angles of 90°, and
- the C–H bond lengths will be different as they are formed from the overlap of 2s orbital of C with 1s orbital of H, and those of 2p orbitals of C with 1s orbital of H's.

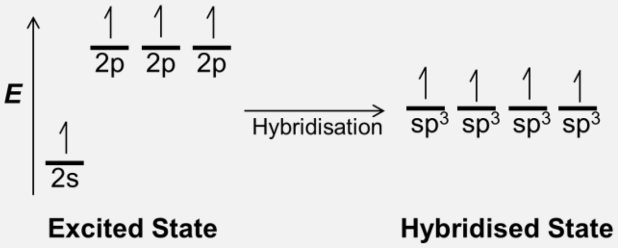
However, each CH_4 molecule is tetrahedral in shape with **4 C–H bonds of equal length directed away from each other at 109.5°**. Thus, the original atomic orbitals of C are **not** used to form the C–H bonds.

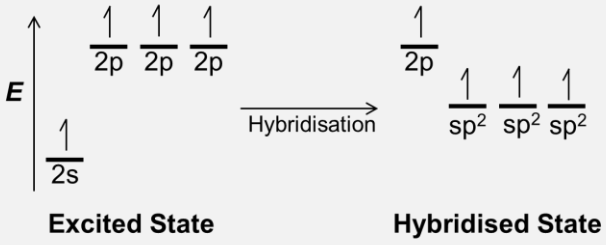
To explain the actual observed shape of CH_4, the hybridisation model was proposed to explain why C–H bonds are equivalent and how the orbitals are made equivalent.

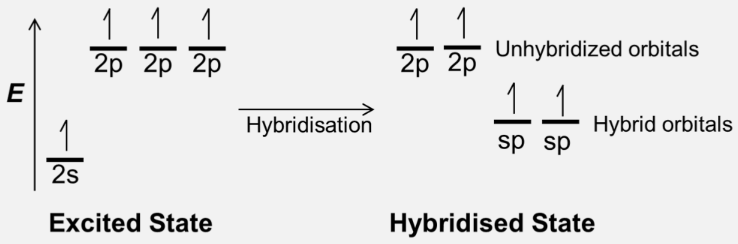
Due to hybridization, orbitals of same energy are formed which gave rise to the respective observed geometry. A central atom can be sp, sp^2 or sp^3 hybridised depending on the geometry around the central atom.

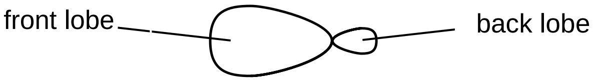
No. of atomic orbitals mixed = No. of hybrid orbitals formed

Hybrid orbitals take part in sigma (σ) bonding only. Pi bonds (π) are formed by unhybridised p orbitals.

sp^3	The four orbitals then mix to give **four equivalent sp^3 hybrid** orbitals. The four sp^3 hybrid orbitals are equivalent in energy and are arranged as far apart as possible in a **tetrahedral** geometry to minimise repulsion between electrons. 

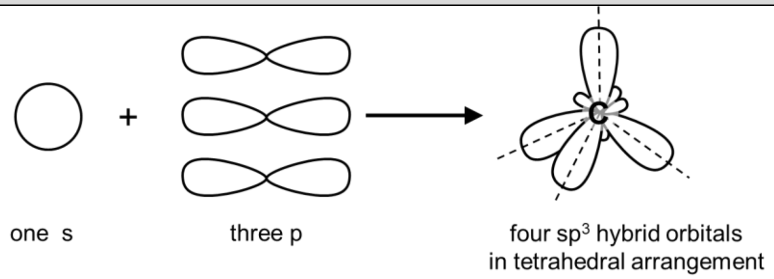
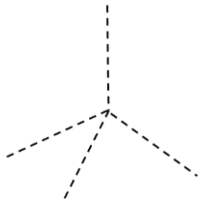
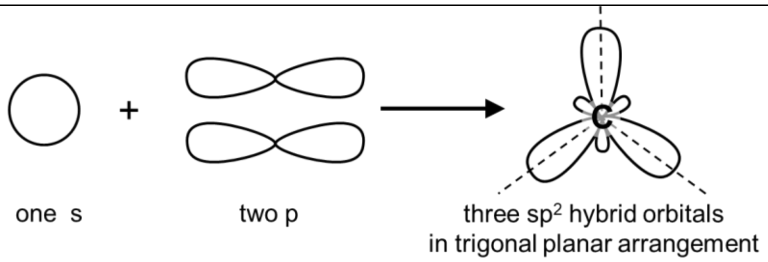
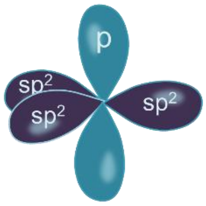
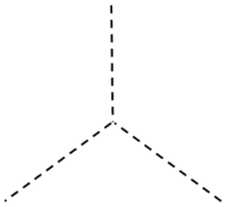
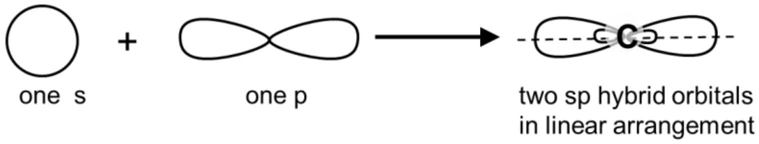
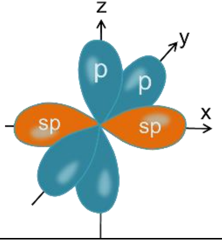
sp^2	Since there are only **three bonds** around each C, only **three sp^2 hybrid** orbitals are formed. One of the 2p orbitals remains unhybridised. The three sp^2 hybrid orbitals are equivalent in energy and arranged in a **trigonal planar** geometry as far apart as possible to minimise repulsion between electrons. 

sp	2s orbital and one of the 2p orbitals of each C mix to form **two sp** hybrid orbitals. The remaining two 2p orbitals remain are unhybridised. 



General shape of sp^3 / sp^2 / sp hybrid orbital

In the formation of covalent bonds, only the front lobe is used to overlap with an orbital of another atom by convention.

Total no. of electron regions	**Hybridisation of central atom**	**Formation of hybrid orbitals and arrangement of hybrid orbitals <u>around</u> the central atom**	**<u>Let's practice!</u>**
4	**sp^3** (s^{1}p^3)	 	
3	**sp^2** (s^{1}p^2)	 **Note: There is one unhybridised p orbital for π bonding** 	
2	**sp** (s^{1}p^1)	 **Note: There are two unhybridised p orbitals for π bonding** 	

Important note:

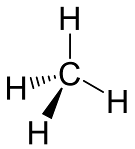
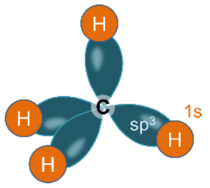
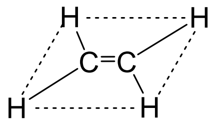
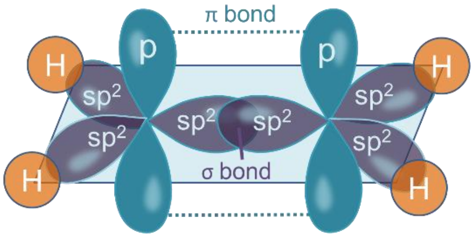
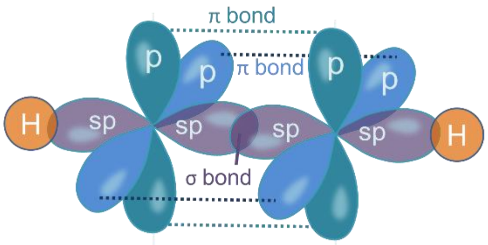
(a) Identify the type of hybridisation based on the electron pair geometry.

(b) The following table shows the percentage of "s" character in the three types of hybrid orbitals

Type of hybrid orbitals	% of "s" in hybrid orbitals
sp^3	25
sp^2	33.3
sp	50

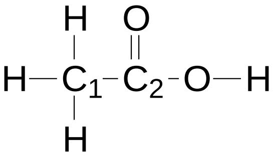
Hybrid orbitals with higher % of "s" character overlap to form a stronger bond.

Hybridisation of Carbon in Organic compounds

<u>sp^3 hybridisation</u> Methane, CH_4 **tetrahedral** with a bond angle of 109.5°.   	There are 4 electron regions around the C atom of CH_4. → the carbon in CH_4 is sp^3 hybridised (s^{1}p^3) The four sp^3 hybrid orbitals are in **<u>tetrahedral</u>** arrangement around C. Each sp^3 hybrid orbital overlaps head-on with 1s orbital of H to form a sigma (σ) bond.
<u>sp^2 hybridisation</u> Ethene, C_2H_4 Around each C, trigonal planar with bond angle of 120°   (Diagram to illustrate how the orbitals overlap in ethene, **<u>you are not required</u>** to reproduce this drawing for A level)	There are 3 electron regions around the C atom of C_2H_4. → Both the carbon atoms in C_2H_4 are sp^2 hybridised (s^{1}p^2) The three sp^2 hybrid orbitals are in **<u>trigonal planar</u>** arrangement around C. The C–H sigma (σ) bond is formed by **<u>head-on</u>** overlap between sp^2 hybrid orbital of C with 1s orbital of H The C=C bond is formed by i) one sigma (σ) bond **<u>head-on</u>** overlap between sp^2 hybrid orbital of C_1 with sp^2 hybrid orbital of C_2. ii) one pi (π) bond **<u>sideway</u>** overlap between unhybridised 2p orbital of C_1 with unhybridised 2p orbital of C_2
<u>sp hybridisation</u> ethyne, C_2H_2 Around each C, linear with bond angle of 180° H—C≡C—H  (Diagram to illustrate how the orbitals overlap in ethyne, **<u>you are not required</u>** to reproduce this drawing for A level)	There are 2 electron regions around the C atom of C_2H_2. → Both the carbon atoms in C_2H_2 are sp hybridised (s^{1}p^1) The two sp^2 hybrid orbitals are in **<u>linear</u>** arrangement around C. The C–H sigma (σ) bond is formed by **<u>head-on</u>** overlap between sp hybrid orbital of C with 1s orbital of H The C≡C bond is formed by i) one sigma (σ) bond **<u>head-on</u>** overlap between sp hybrid orbital of C_1 with sp hybrid orbital of C_2. ii) **<u>two</u>** pi (π) bond **<u>sideway</u>** overlap between unhybridised 2p orbital of C_1 with unhybridised 2p orbital of C_2

Checkpoint 3

1. What is the type of hybridisation present in C_1 and C_2 in ethanoic acid shown below?



	C_1	C_2
A	sp^2	sp^2
B	sp^2	sp^3
C	sp^3	sp^2
D	sp^3	sp^3

2. Which statement is correct for the hydrocarbon $CH_2=CHCH_2CH=CH_2$?

A all C atoms are sp^2 hybridized.

B one C atom is sp^3 hybridized.

C there are two sp hybridized C atoms.

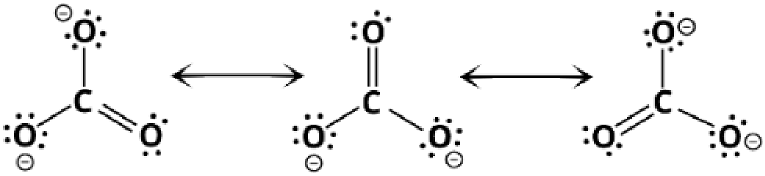
D the two terminal C atoms are sp^3 hybridized.

3. Use a labelled diagram to show the orbitals that form the C=C bond in $CH_2=CH_2$.

1.4.2 Delocalisation of electron (Resonance structures)

Some molecules/ions cannot be adequately represented by a single structure.

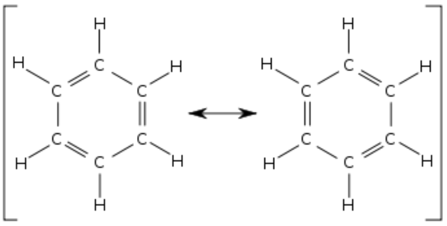
Consider the anion CO_3^{2-}, three structures are possible:



The three structures are called canonical structures. They have the same placement of atoms and σ bonds but different arrangement of π bonds.

A molecule/ion exhibits resonance when there is **continuous overlap of p orbitals over at least 3 adjacent atoms**, allowing for **delocalisation of π electrons**.

Delocalisation of electron in benzene (C_6H_6)



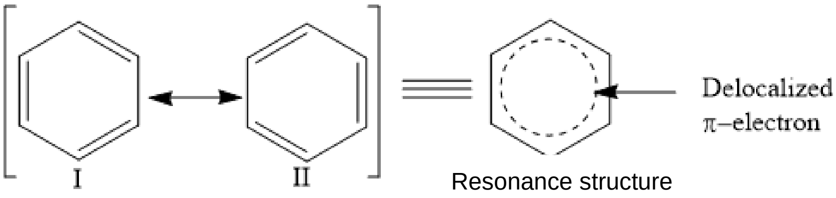
The two canonical structures of C_6H_6 above each contains three C–C single bond and three C=C double bonds. If any one of the above structures of benzene is accurate, the C=C bond will be shorter and stronger than the C–C bond.

Experimentally, it is observed that the carbon-carbon bond energy in benzene is different from a C−C single bond and a C=C double bond.

In fact, the six C−C bond lengths in benzene are identical (intermediate between a single and double bond).

Experimental data:

Bond	Bond Energy /kJ mol^{-1}	Bond order
C–C	350	1
C=C	610	2
C$\overset{\cdots}{-}$C *(benzene)*	*520*	*1.5*



The six carbon atoms in the benzene molecule are **sp^2 hybridised**. Each carbon atom has an unhybridised p orbital containing one electron. The **six unhybridised p orbital in benzene overlap continuously**, allowing for **delocalisation of six π electrons**.

This gives rise to a resonance hybrid structure with **partial double bond character** (intermediate between single and double bond) for the carbon-carbon bonds.

1.5 REACTIONS INVOLVING ORGANIC COMPOUNDS

Success Criteria:

- I understand that in a bond forming process between 2 reacting particles, it involves the flow of electrons from electron-rich to electron-poor sites.

All chemical reactions involve the transfer of electrons resulting in bond breaking or forming. Reactions of organic compounds involve the breaking and forming of covalent bonds in order to make desirable and useful organic molecules.

The illustration of electron movements to explain the repertoire of bond breaking and formation in synthesizing an organic molecule is known as **mechanism**.

Electron Flow in Reaction Mechanism

Movement of electron pair (2 electrons) is illustrated using **full curly arrow** originating from **the electron-rich to the electron-poor sites**.

Nucleophiles (“Nucleus loving”)	**Electrophiles (“Electron loving”)**
● are electron rich species (contain π bonds or lone pair of electrons available for donation) that can **donate** an electron pair to an electron-deficient species.	● are electron-deficient species that can **accept** an electron pair from an electron-rich species.
• can be neutral molecules with lone pair electron (e.g. H_2O, NH_3)	● can be atoms which carry partial positive charge (e.g. $^{\delta+}Br$ in Br_2, $^{\delta+}H$ in HBr)
• or negatively charged ions (anions) (e.g. OH^-, CN^-).	● or positively charged (cations) (e.g. $^+CH_3$, Br^+)
	● or atom that has an empty orbital in the valence shell (e.g. A*l* in A*l*C*l*$_3$).

Success Criteria:

- I can explain and use the terms: homolytic fission and heterolytic fission.
- I can use arrows (half head curly arrow or full head curly arrow) to show transfer of electrons during bond breaking or bond forming processes

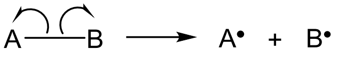
1.5.1 Bond Fission (bond breaking)

There are 2 ways in which bonds can be broken.

Note:
Arrows are used to illustrate movement of electrons. The arrowhead shows where the electrons are being transferred to.
Arrows always** start from the regions of a **higher electron density to a lower electron density.

Half head curly arrow (⌒) represents movement of a single electron.

- **Homolytic fission** (homolysis)

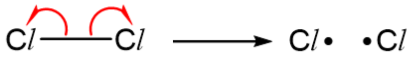


Each atom gains 1 e^- from the bond

Radicals

When the two bonding atoms are of relatively similar electronegativities, the two shared electrons in the covalent bond can be split equally between the two atoms so that each atom acquires one of the bonding electrons, forming free radicals (species with unpaired electron).

e.g. Formation of chlorine radical

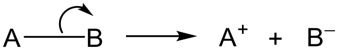


A free radical

- contains an **unpaired** (**lone**) electron.
- is extremely reactive because the odd electron readily combines with an electron in another atom to form a covalent bond.

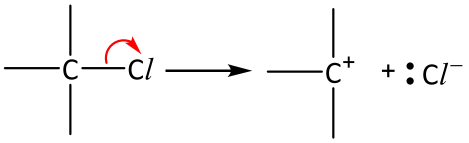
Full head curly arrow (⌒) represents the movement of a pair of electrons.

- **Heterolytic fission** (heterolysis)



Both e^- in the bond is transferred to atom B.

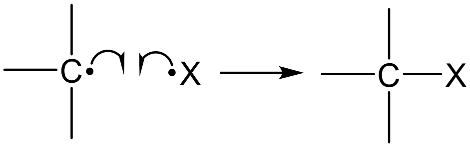
When the two bonding atoms are of different electronegativities, the two shared electrons in the covalent bond are split unequally between the two atoms such that the **more** electronegative atom acquires **both** of the bonding electrons, forming an **anion**, while the **less** electronegative atom forms a **cation**.

Formation of a carbocation	**Carbocation**
	Each contains a carbon bearing a **positive** charge. The **positively-charged** C has **only six** electrons in its valence shell and is electron-deficient.

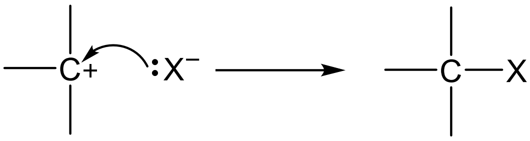
1.5.2 Bond formation

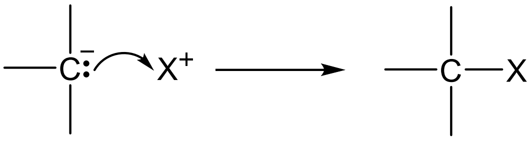
- Two radicals collide to form a stable product.

Take note of the arrows used and the direction!



- An electron-rich region donates an electron pair to an electron-deficient region.

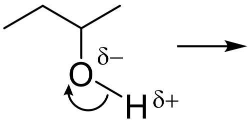




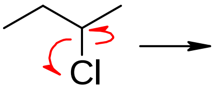
Checkpoint 4

Draw the structure of the product formed from the proposed mechanism.

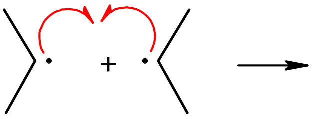
(a)



(b)

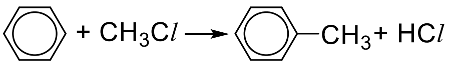
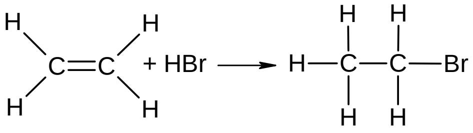
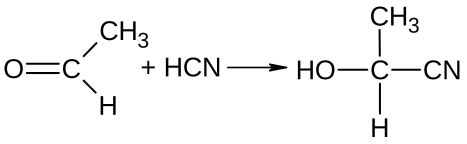
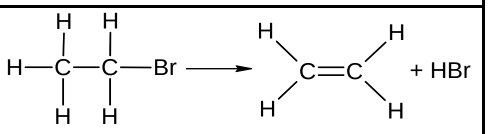
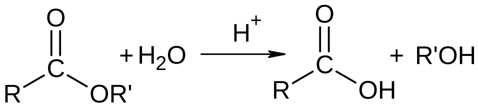
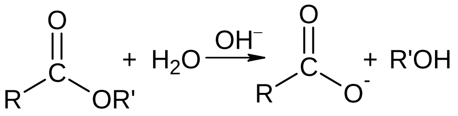
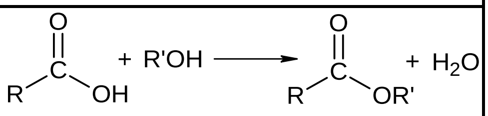
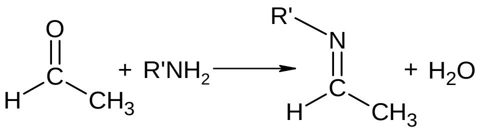


(c)



1.5.3 Types of Organic Reactions

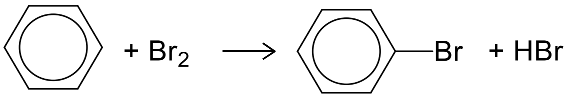
Success Criteria:
- I can identify the type of organic reaction by looking at the changes in the organic molecule in a given equation.

Type of reaction	*Characteristics*	*Examples*
Substitution	● An atom or a group of atoms is **substituted** (replaced) by another atom or group of atoms	$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ One H of methane is substituted by a Cl atom.  One H of benzene is substituted by a methyl group.
Addition	● Occurs only when there is unsaturation in reactant molecule (double or triple bonds) ● Two species react to form a single product without any elimination of atom	 
Elimination	● The reverse of addition reactions ● Atoms or a group of atoms are removed to form a product molecule with a **double bond**	
Hydrolysis	● “Hydro” means water and “-lysis” means breaking. ● A reaction in which a molecule is spilt into 2 or more smaller species by the action of water ● An acid or alkali is often used as catalyst	 
Condensation	● The reverse of hydrolysis ● **Two molecules** react to form a **bigger molecule** with the elimination of a small molecule, e.g. H_2O	 

Type of reaction	***Characteristics***	***Examples***
Oxidation	• 1 or more **O** is **added** to the molecule *and/or* • 1 or more **H** is **removed** from the molecule	$CH_3CH_2OH + 2\mathbf{[O]} \rightarrow CH_3CO_2H + H_2O$ $CH_2{=}CH_2 + 6\mathbf{[O]} \rightarrow 2CO_2 + 2H_2O$ In balancing an organic redox equation, the symbol **[O]** is used to denote each O contributed by the oxidising agent such as $KMnO_4$ or $K_2Cr_2O_7$. "O_2" is used if the oxidising agent is O_2.
Reduction	• 1 or more **O** is **removed** from the molecule *and/or* • 1 or more **H** is **added** to the molecule.	$CH_3CO_2H + 4\mathbf{[H]} \rightarrow CH_3CH_2OH + H_2O$ In balancing an organic redox equation, the symbol **[H]** is used to denote each H contributed by the reducing agent such as $LiAlH_4$ or $NaBH_4$. "H_2" is used if the reducing agent is H_2.

Checkpoint 5

Classify each of the following organic reactions as a substitution, addition, elimination, hydrolysis, condensation, oxidation or reduction reaction.

1	$CH_3COOH + CH_3CH_2OH \longrightarrow CH_3COOCH_2CH_3 + H_2O$	
2		
3	$CH_3CHBrCH_2CH_3 \xrightarrow{OH^-} CH_3CH{=}CHCH_3 + HBr$	
4	$CH_2{=}CHCH_3 + 5[O] \longrightarrow CH_3CO_2H + CO_2 + H_2O$	

CONCEPTS IN INTRODUCTION IN ORGANIC CHEMISTRY			
	Success Criteria	Relevant Tutorial Question	What do you still struggle with? Write your queries here.
	I am able to:		
(a)	Interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound: (i) hydrocarbons (ii) halogen derivatives (iii) hydroxyl compounds (iv) carbonyl compounds (v) carboxylic acids and derivatives (vi) nitrogen compounds	CP1, Tut Qn 2, 3	
(b)	Name organic compounds using IUPAC convention	CP2, Tut Qn 1, 3	
(c)	Describe sp^3 hybridisation, as in ethane molecules, sp^2 hybridisation, as in ethene molecules, and sp hybridisation, as in ethyne molecule.	CP3, Tut Qn 4, 5 and 6	
(d)	Explain the shapes of, and bond angles in, the ethane, ethene and ethyne molecules in relation to σ and π carbon-carbon bonds	CP3	
(e)	Recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron-poor sites	CP4, Tut Qn 9 and 10	
(f)	Interpret, and use the following terms associated with organic reactions (i) Homolytic and heterolytic fission (ii) Carbocation (iii) Free radical, electrophile, nucleophile (iv) Substitution, addition, elimination, condensation, hydrolysis (v) Oxidation and reduction	CP5, Tut Qn 7 and 8	

1 INTRODUCTION TO ORGANIC CHEMISTRY TUTORIAL

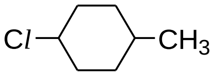
Structure and naming

1 Give the IUPAC name for each compound.

(a) $CH_3CH(CH_3)CH_2CH(OH)CH_3$

(b) $CH_2{=}CHCH{=}CHBr$

(c)



(d) $CH_3CH(CO_2H)CH_2CH_3$

2 Draw the skeletal formula of each compound.

(a) 2,2,4-trimethylhexane

(b) 2,4-dibromomethylbenzene

(c) 1-ethyl-3,3-dimethylcyclopentane

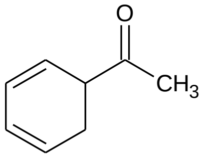
3 For each part, the name given is **incorrect**. Draw the skeletal formula for each and give its correct IUPAC name.

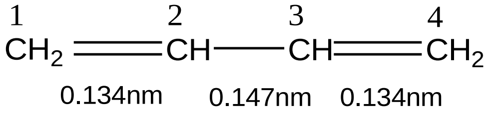
(a) 2-ethylpentane

(b) 2-chloro-2-ethylbut-3-ene

(c) 2,3-diethylcyclopentane

(d) 1,1-dimethy-3-propylhexane

Hybridisation						
4	State the type of hybridisation of **each carbon** in each species.					
	(a)	CH_3^-	**(b)**	CH_3CH_2OH	**(c)**	CH_3CHO
	(d)	CH_3^+	**(e)**			

5	[N08/I/19] The bond lengths in buta-1,3-diene differ from those which might be expected. The carbon-carbon bond length in ethane is 0.154nm and in ethene is 0.134nm. The central single bond in buta-1,3-diene (C2-C3), however, is shorter than the single bond in ethane: it is 0.147nm. $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$ 0.134nm 0.147nm 0.134nm What helps to explain this C2-C3 bond length?	
	A	It is a sp^2-sp^2 overlap.
	B	It is a sp^2-sp^3 overlap.
	C	The electrons in the filled p orbitals on C2 and C3 repel each other.
	D	The sp^3-sp^3 bonding is pulled shorter by a p-p (π bond) overlap.
6	Methanal has the molecular formula of HCHO and contains an unsaturated carbon. The C=O functional group of methanal can be described as being joined by a **σ-bond** and a **π-bond**.	
	(a)	Identify the type of hybridisation of C in methanal.
	(c)	Hence, use a labelled diagram to show the orbitals that form the C=O bond in methanal.

Type of reaction

7 Classify each reaction as ***addition***, ***elimination***, ***condensation, oxidation***, ***reduction*** or ***substitution***.

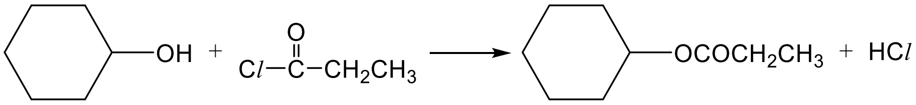
(a) $CH_3CH_3 + Br_2 \longrightarrow CH_2BrCH_3 + HBr$

(b) $CH_2{=}CHCH_3 + Br_2 \longrightarrow BrCH_2CH_2BrCH_3$

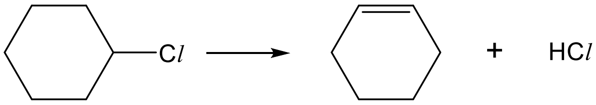
(c) $CH_3CH_2CH_2OH + 2[O] \longrightarrow CH_3CH_2CO_2H + H_2O$

(d) $CH_3CO_2H + 2[H] \longrightarrow CH_3CHO + H_2O$

(e)



(f)



Balancing equation for organic redox reaction

8 Balance each equation with either [O] or [H]. Add H_2O whenever necessary.

(a) $CH_3CH_2OH \longrightarrow CH_3CHO$

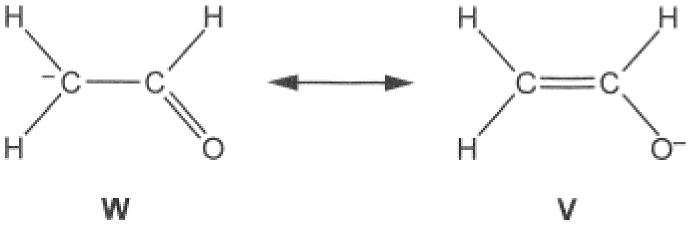
(b) $CH_3CH_2CONH_2 \longrightarrow CH_3CH_2CH_2NH_2$

(c) $CH_3CH{=}CHCH_3 \longrightarrow 2CH_3CO_2H$

(d) $CH_3CO_2CH_3 \longrightarrow CH_3CH_2OH + CH_3OH$

Drawing Resonance Structures

9 [N22/P2/5d(i) and (ii)]
The enolate ion can be represented by two different structures, W and V, as shown in the figure below. The arrow ↔ indicates that the actual structure of the enolate ion is somewhere between these two structures, with the negative charge delocalised over both the oxyen and carbon atoms.



(a) Sugges how the delocalisation of electrons occur in an enolate ion.

(b) Deduce the number of delocalised electrons in an enolate ion.

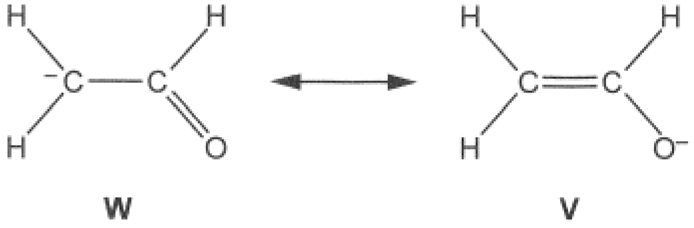
Electron flow in Reaction Mechanism

10 [N22/P3/3e]
Benzoyl peroxide, $(C_6H_5CO)_2O_2$, can be used to treat some skin conditions. It can be prepared by treating benzoyl chloride with barium peroxide.

$$2C_6H_5COCl + BaO_2 \rightarrow (C_6H_5CO)_2O_2 + BaCl_2$$

The O–O bond in peroxide is weak and undergoes homolytic fission.

Use curly arrow notation to show the equation for the homolytic fission of $(C_6H_5CO)_2O_2$



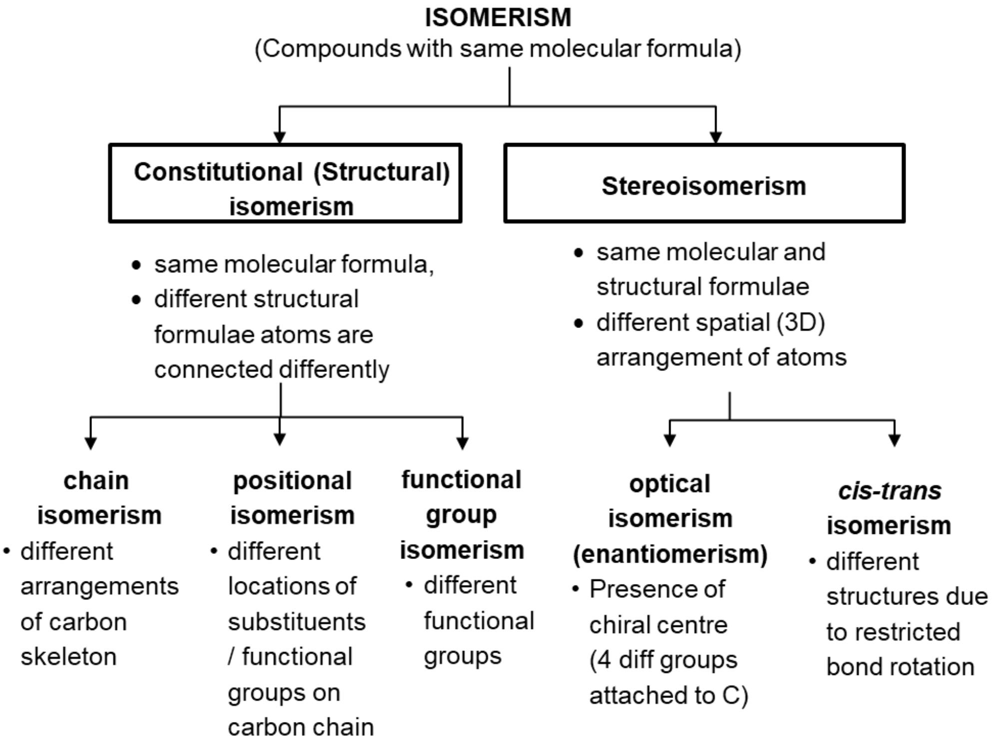
2 ISOMERISM

2.1 INTRODUCTION

Isomerism refers to the **existence of two or more stable compounds** with the **same molecular formula** but **different arrangement** of the **atoms**. These compounds are known as **isomers.**

Note: bonds have to be broken in order for isomer A to be converted to isomer B.

There are 2 **major** types of isomerism: **constitutional (structural) isomerism** and **stereoisomerism.**



2.2 STRUCTURAL ISOMERISM (CONSTITUTIONAL ISOMERISM)

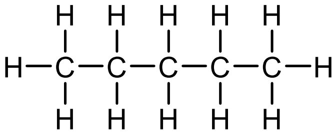
Success Criteria:

- I can describe and draw constitutional (structural) isomers

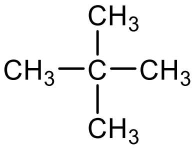
Structural isomers have the **same molecular formula** but **different structural formulae**; i.e., at least one atom is bonded to a different atom in one isomer compared to another.

(i) Chain Isomers

e.g. structural isomers of C_5H_{12}



Pentane (b.p. 36 °C)

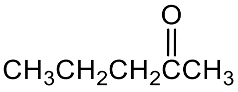


2,2-dimethylpropane (b.p. 10 °C)

Both share the same molecular formulae but differ in the longest continuous hydrocarbon chain.

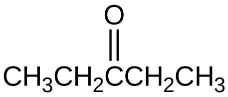
(ii) Positional Isomers

e.g. pentan-3-one vs pentan-2-one



$CH_3CH_2CH_2\overset{O}{\overset{||}{C}}CH_3$

pentan-2-one



$CH_3CH_2\overset{O}{\overset{||}{C}}CH_2CH_3$

pentan-3-one

Both share the same molecular formulae but different location of C=O group on the longest continuous hydrocarbon chain.

Chain and position isomers have **different physical properties** such as density, solubility, melting and boiling points as the **surface area of contact between molecules** are different.

These isomers have **similar chemical properties** as they have the same functional groups.

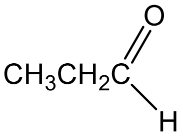
However, the shape of a molecule often determines its chemical reactivity. An easy-to-reach functional group or other side chain reacts more readily than one that experiences **steric hindrance.** (i.e., one that is "buried" in the middle of a long C chain or "protected" by bulky groups). *(Concept of steric hindrance will be covered in details in later chapter.)*

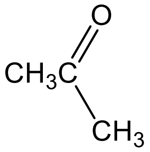
(iii) Functional group isomers

There are **4 common pairs of functional group** isomers.

- alcohols and ethers with general formula $C_nH_{2n+2}O$
  CH_3CH_2OH, ethanol and CH_3OCH_3, dimethyl ether

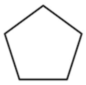
- aldehydes and ketones with general formula $C_nH_{2n}O$



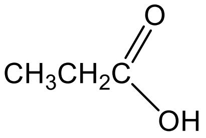


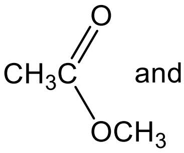
- alkenes and cycloalkanes with general formula C_nH_{2n}

$CH_3CH_2CH_2CH=CH_2$

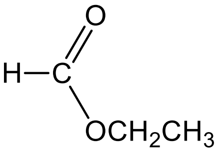


- Carboxylic acids and esters with general formula $C_nH_{2n}O_2$





and



Functional group isomers have **different** physical and chemical properties.

Note:
Consider
1) chain isomerism
- vary no. of C atom in longest chain by moving C atoms to become substituent (e.g. branch)

2) positional isomerism
- vary positional number of principal functional group and substituents

3) functional group isomerism
-vary arrangement of atoms into a different functional group

Checkpoint 1

(a) Draw all the structural isomers of molecular formula C_6H_{14}.

(b) Draw all the structural isomers of an ester of molecular formula $C_4H_8O_2$.

2.3 STEREOISOMERISMS

Stereoisomers have the same molecular and structural formulae. The corresponding atoms are bonded to the same atoms but differ in the spatial (3D) arrangements of their bonds. There are two types of stereoisomerisms:
cis-trans isomerism and optical isomerism (enantiomerism).

2.3.1 Cis-trans Isomerism

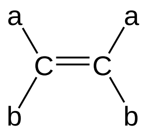
Success Criteria:

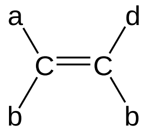
- I can state the two structural features required for an alkene to undergo cis-trans isomerism.
- I can name and draw cis- and trans- isomers.

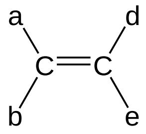
Two conditions are required for cis-trans isomerism to exist:

- restricted rotation about a bond can be due to (i) C=C bonds in a straight chain) (ii) a ring structure (not in H2 syllabus)
- two different groups on **<u>each</u>** of the carbon atoms with restricted rotation.

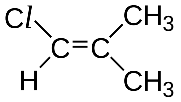
e.g.





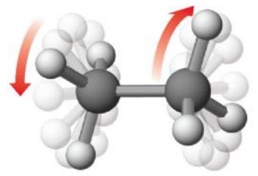
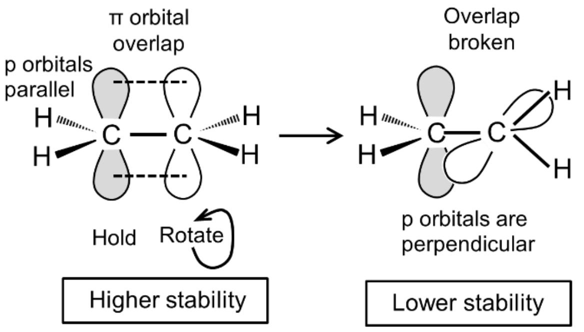
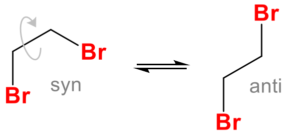
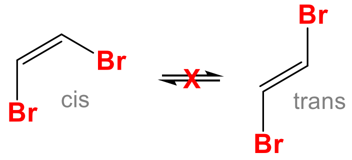


The compound below does not exhibit cis-trans isomerism as it has two methyl groups attached to one of the C atoms in the C=C bond.

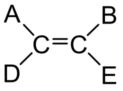


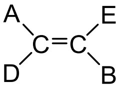
(i) Restricted rotation about single bonds versus double bonds

Note:
Free rotation about the single C–C bond may cause spatial arrangement of atoms across 2 C to differ but they are not isomers of each other as bond breaking process is not involved to convert 1 arrangement to the other.

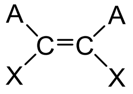
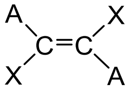
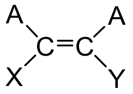
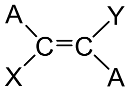
Single bond	Double bond
	
Free rotation is possible about σ bonds. Rotation does not cause any bond to be broken. 	Free rotation is not possible about a double bond.  Conversion of cis-isomer to trans-isomer requires the π bond to be broken

Note:
Alkenes with four different substituents across C=C also exhibit cis-trans isomerism. Another naming convention (E / Z) is used instead.
**E/Z naming is not in H2 syllabus.





(ii) Naming of cis-trans Isomers

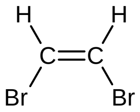
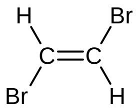
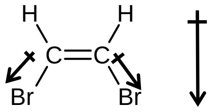
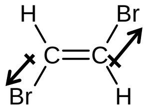
***cis*-isomers**	***trans*-isomers**
have identical atoms / groups of atoms on the **<u>same</u>** side of the double bond	have identical atoms / groups of atoms on diagonally **<u>opposite</u>** sides of the double bond
e.g. 	
e.g. 	

(iii) Properties of cis-trans isomers

Success Criteria:
- I can explain why cis- and trans- isomers have different boiling and melting points

*Cyclic alkenes do not exhibit cis-trans isomerism despite satisfying both structural features required. (see 2.3.1.)

Cis-trans isomers have the same chemical but different physical properties.

	cis-isomer	trans-isomer
Structural Formula		
Net Polarity	 polar molecule	 non-polar molecule
Boiling Point	has a higher boiling point as more energy is needed to overcome stronger permanent dipole-permanent dipole interactions between the molecules	has a lower boiling point as less energy is needed to overcome weaker intermolecular instantaneous dipole-induced dipole interactions
Melting Point	has lower melting point due to poorer packing efficiency (lesser number of molecules per unit volume in solid state), leading to less intermolecular forces to overcome per unit volume	has a higher melting point due to better packing efficiency of molecules (packs better in a crystalline lattice due to its more symmetrical shape), leading to more intermolecular forces to overcome per unit volume

(iv) Molecules containing two or more cis-trans C=C

In general, a molecule with **“m” cis-trans C=C** has a maximum of **2^m** stereoisomers.

For a compound with three cis-trans C=C, eight (2^3) stereoisomers are expected.

2.3.2 Optical Isomers

Success Criteria:

- I can identify a chiral centre.
- I can use suitable diagrams to illustrate optical isomerism and state the properties of optical isomers.
- I understand the term racemic mixture and able to explain why it is optically inactive.
- I can deduce whether a molecule is chiral by checking for the (i) presence of chiral centre and (ii) plane of symmetry.

Optical isomerism exists when molecules contain at least one chiral centre causing them to lack both a point and plane symmetries.

(i) Chirality

Video on Chirality

Time: 0:38 – 2:08

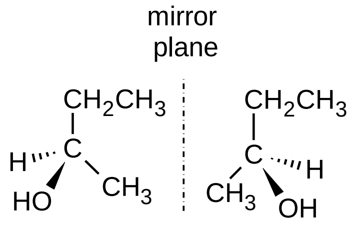
https://tinyurl.com/aasmpfj7

A molecule is described to contain a ‘**chiral** centre’ if it has a carbon atom attached with four different atoms / groups of atoms. As a result, the mirror images of the molecules are non-superimposable.

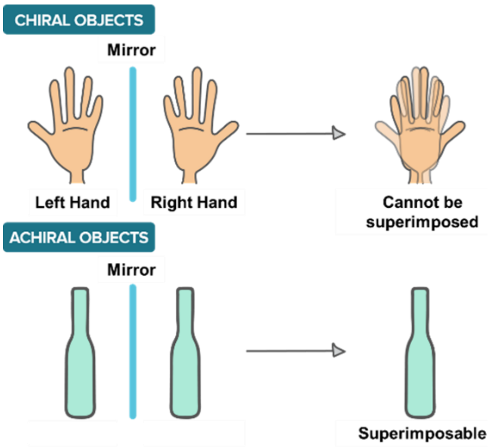
A chiral carbon is usually labelled with an asterisk (*).

Enantiomers refer to a pair of compounds with the same connectivity but opposite three-dimensional shapes. Enantiomers are non-superimposable mirror images of each other.

e.g. a molecule with a chiral centre with its enantiomer



enantiomers / non-superimposable mirror images



Obtained from https://www.khanacademy.org/

(ii) Properties of optical isomers (enantiomers)

Enantiomers:

- rotate the plane of plane-polarised light by equal angles but in **opposite** directions when equal concentration of enantiomers are being analysed.
- have **similar chemical properties** (except in their interactions with another chiral molecule).
- have **similar physical properties** (except in the direction in which they rotate plane-polarised light).
- have different biological properties.

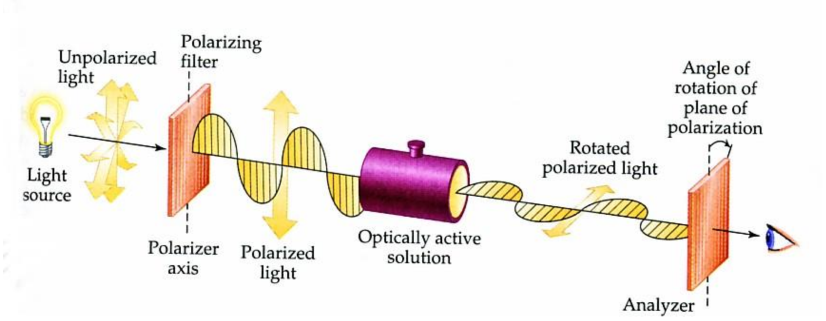
(iii) Racemic mixture

In a mixture that contains **equal concentrations of enantiomers**, the equal but opposite rotation of plane-polarised light by each enantiomer results in net zero optical activity. Such a mixture is termed a **racemic mixture (racemate)**. The mixture becomes **optically inactive** (does not rotate plane of plane-polarised light) despite having chiral molecules.

Note:
It is not possible to know which optical isomer rotates the plane polarized light clock-wise or anti-clockwise unless an experiment is carried out.

PLANE-POLARISED LIGHT (*For info only, not in H2 syllabus*)

Light is a wave vibrating in all planes at right angles to the direction of its propagation. Light vibrating in all possible planes is said to be unpolarised. Plane-polarised light, composed of waves that vibrate in only one plane, can be produced by passing unpolarised light through a polariser.



The rotation of the plane of plane-polarised light by an optically active compound can be measured by a polarimeter.

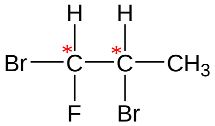
- The enantiomer which rotates polarised light to the right is termed dextrorotatory (D or (+) form).
- The enantiomer which rotates polarised light to the left is termed laevororotatory (L or (-) form).

(iv) Molecules containing two or more chiral centers

In general, a molecule with **n chiral centers** has a maximum of **2^n** stereoisomers.

For a compound with two chiral centers, four stereoisomers are expected.
total no. of stereoisomers = $2^2 = 4$

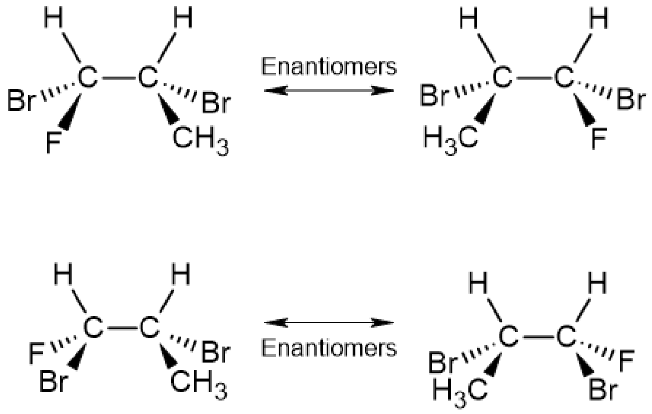
e.g.



$$Br-\overset{H}{\underset{F}{\overset{*}{C}}}-\overset{H}{\underset{Br}{\overset{*}{C}}}-CH_3$$

Video on drawing Enantiomers

3D structures of stereoisomers:

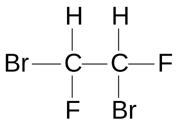


Video on
Meso Compound

https://tinyurl.com/
mesocompound

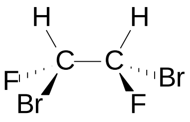
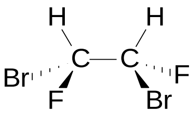
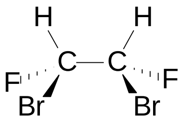
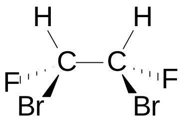
However, there are some molecules with 2 chiral centers with less than 4 stereoisomers.

e.g.



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ Br- & C & - & C & -F \\ & | & & | & \\ & F & & Br & \end{array}$$

Theoretical: total no. of stereoisomers = $2^2 = 4$
Actual: total no. of stereoisomers = $4 - 1 = 3$

Isomer **A**	Isomer **B**
	
Isomer **C**	Isomer **D**
	

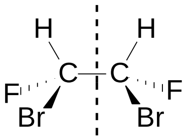
Isomers **A** and **B** are enantiomers (non-superimposable mirror images).

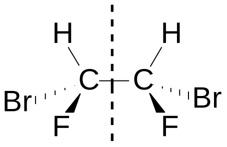
Isomers **C** and **D** are identical (superimposable mirror images). **C** or **D** is known as a meso compound.

Hence, this molecule has a total of only <u>**three**</u> stereoisomers despite having 2 chiral centres.

(v) Meso compound

A meso compound is one that contains two chiral centers but is superimposable on its mirror image as it has a plane of symmetry.





A meso compound is optically inactive as the effect on the plane-polarised light by each half of the molecule is equal in magnitude but opposite in directions. Hence, they cancel each other to give a net zero effect on plane-polarised light.

2.3.3 Molecules that exhibit both cis-trans and optical isomerism

Success Criteria:

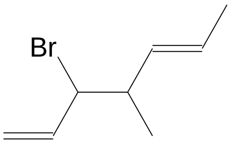
- I can identify chiral centres and/or cis-trans isomerism in a molecule of a given structural formula.
- I can deduce the maximum possible number of isomers using 2^{m+n}.

Note:
Stereoisomerism refers to BOTH cis-trans isomerism and optical isomerism

In general, a molecule with **m** C=C bonds that exhibit cis-trans isomerism and **n** chiral centers has a maximum of $\mathbf{2^{m+n}}$ stereoisomers.

Worked Example 1

What is the total number of stereoisomers for the following compound?

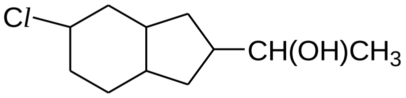


2 chiral carbon and 1 cis-trans C=C

Total number of stereoisomers = 2^3 = 8

Worked Example 2

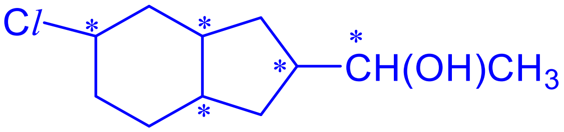
How many chiral carbons are present in the molecule below? Label each chiral C with *.



To identify chiral carbon in skeletal formula,

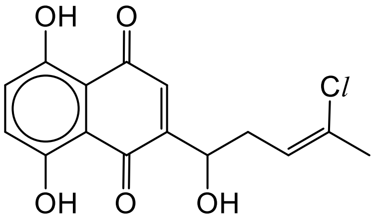
1) look out for intersections of 3 single bonds (4th bond is C−H that is not drawn) or 4 single bonds

2) Check there are 4 unique groups bonded to the carbon.



Checkpoint 2

(a) How many stereoisomers are there in the following compound?



A 2 **B** 4 **C** 6 **D** 8

(b) State and explain clearly the type of stereoisomerism shown by each compound and state the total number of stereoisomers, if any.

(i) $CH_3CH{=}CHCH_2CH(OH)CH_3$

(ii) $(CH_3)_2C{=}CHCH_2CH(OH)CH_2CH{=}C(CH_3)_2$

(iii)

2.4 Biological Properties of Optical Isomers (Enantiomers)

Success Criteria:

- I can recognize different stereoisomers exhibit different biological properties, for example in drug action.

The small difference in the spatial arrangement of atoms between a pair of enantiomers may seem trivial and unimportant to you and me but to **living organisms** this difference is critical. Cells and enzymes recognise these differences and **often can use only one of the enantiomers**.

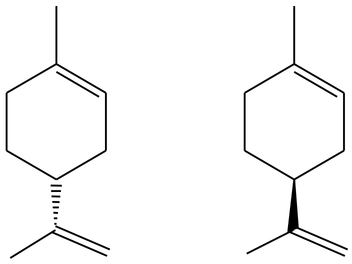
Below are some examples.

The proteins in our bodies are built from only one enantiomer of each amino acid.

Enantiomers can interact differently with the chiral receptor cells in the taste buds on our tongue, leading to different tastes. All D-amino acids taste sweet; their enantiomeric counterparts are either tasteless or bitter.

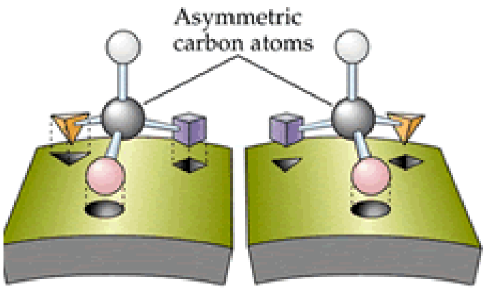
Enantiomers can interact differently with the chiral receptor cells in our nose, leading to different smells.

enantiomers of limonene



found in oranges found in lemons

Drugs work by interacting with the appropriate receptor site via intermolecular interactions. The interactions are very specific. Treating the patient with the wrong enantiomer of a drug can at best be harmless; at worst can harm the patient even further.



Hence, it is important that optically pure compounds are synthesised and administered. However, **racemic mixtures are usually obtained in normal laboratory syntheses**. Further isolation and purification are required to obtain the desired isomer.

Pharmaceutical companies devised enantioselective synthesis to prepare only the single enantiomer. It is also important to test the target compound under physiological conditions to ensure it does not undergo racemisation.

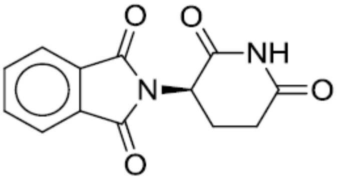
Stereoisomerism in the Real-World (For info only)

Video on Thalidomide

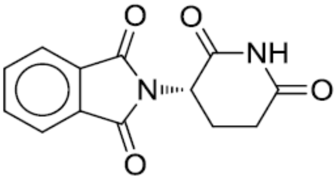
https://tinyurl.com/d9jpkb7h

Thalidomide, was released into the market in 1957 in West Germany to treat morning sickness in pregnant women. Shortly after the drug was sold, in Germany, between 5,000 and 7,000 infants were born with malformation of the limbs. Later it was found that of the two enantiomers, (+)-thalidomide has the desired sedative effect, while (–)-thalidomide possesses the undesirable teratogenic effects (caused birth defects).

However, the enantiomers can interconvert in vivo (in the human body), so if a human is given pure (+)-thalidomide or (-)-thalidomide, both isomers will be present in the body eventually. Therefore, even administering the (+) isomer will NOT prevent the teratogenic effects in humans.



(+)-thalidomide



(–)-thalidomide

Recommended websites

1. http://www.chemguide.co.uk/basicorg/isomermenu.html#top
   (Good notes on the topic and many very good examples.)
2. http://www.chembio.uoguelph.ca/educmat/chm19104/isomers/
   (Interesting problems with 3D animations.)

CONCEPTS IN ISOMERISM			
	Success Criteria	Relevant Tutorial Question	What do you still struggle with? Write your queries here.
	I am able to:		
(a)	Describe constitutional (structural) isomerism	CP1, Tutorial Qn 1 and 2	
(b)	Describe cis-trans isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds	CP2, Tutorial Qn 4,5 and 6	
(c)	Explain what is meant by a chiral centre		
(d)	Deduce whether a given molecule is chiral based on the presence or absence of chiral centers and/or a plane of symmetry	CP2, Tutorial Qn 7,8 and 10 (c).	
(e)	Recognise that an optically active sample rotates plane-polarised light and contain chiral molecules	Tutorial Qn 12 (b), 13 (c)	
(f)	Recognise that enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light		
(g)	Recognise that enantiomers have identical chemical properties except in their interactions with another chiral molecule		
(h)	Recognise that different stereoisomers exhibit different biological properties, for example in drug action	Tutorial Qn 9	
(i)	Deduce the possible isomers for an organic molecule of known molecular formula	Tutorial Qn 3, 10 (c), 14 (b) and (c)	
(j)	Identify chiral centres and/or cis-trans isomerism in a molecule of given structural formula.	Tutorial Qn 7,8, 10 (c), 11 (c) (d), 12 (a), 13 (a) and 14.	

Isomerism Tutorial

Properties of isomers

1 Two organic isomers are known to contain the **same** functional group. Assess the following statements about the two molecules.

(a) They have the same empirical formula. **true / may be true / false**

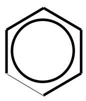
(b) They have the same boiling point. **true / may be true / false**

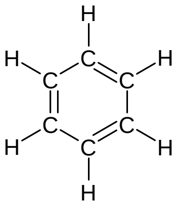
(c) They have the same chemical properties. **true / may be true / false**

(d) They have the same solubility in water. **true / may be true / false**

Constitutional Isomerism (Structural Isomerism)

2 How many isomers of dichlorobenzene are there? (benzene: C_6H_6





)

A 2 **B** 3 **C** 4 **D** 5

3 A halogenoalkane has the molecular formula $C_3H_5Cl_3$.

Which are the possible names of the isomers of this compound?

1 1,1,1-trichloropropane
2 1,2,2-trichloropropane
3 2,2,3-trichloropropane

A **1, 2** and **3** are correct **B** **1** and **2** only are correct

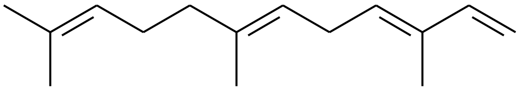
C **2** and **3** only are correct **D** **1** only is correct

Cis-trans Isomerism

4 How many structural and *cis-trans* isomers are there in dichloropropene, $C_3H_4Cl_2$?

A 3 **B** 5 **C** 6 **D** 7

5 *α–Farnesene* is a constituent of the natural wax found on apples. It is also responsible for the characteristic odour of green apples.



α–Farnesene

How many *cis-trans* isomers does this molecule have?

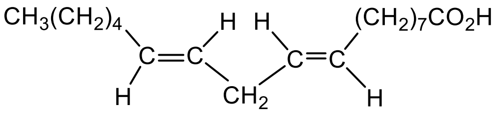
A 2 **B** 4 **C** 8 **D** 16

6 Low fat sunflower spreads which are high in polyunsaturated contain esters of linoleic acid.

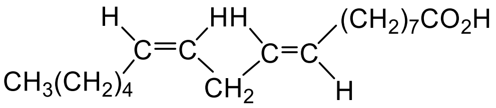
$$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7CO_2H$$

On the lid of a brand of spread, it is claimed that the spread contains virtually no *trans* fatty acid. Which isomer does **not** contain a *trans* linkage that could be present in the spread?

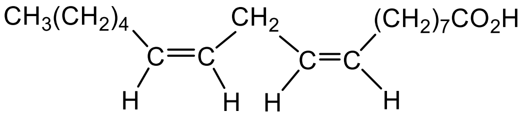
A



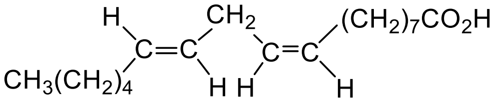
B



C

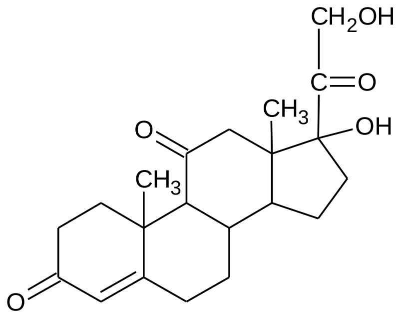


D



Optical Isomerism (enantiomerism)

7 The drug cortisone has the formula shown.

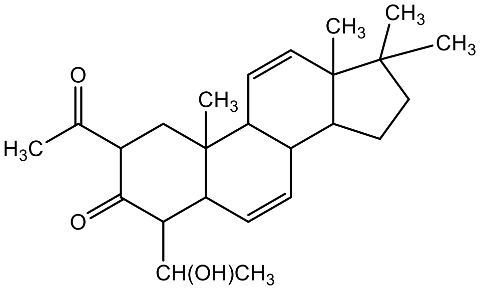


cortisone

How many chiral centers are present in each cortisone molecule?

A 3 **B** 4 **C** 5 **D** 6

8 What is the maximum number of stereoisomers for the molecule shown below?



A 2^8 **B** 2^9 **C** 2^{10} **D** 2^{11}

Answers to Q2-Q

[N22/1/18]

9 The drug ibuprofen has two enantiomers. One enantiomer has the desired pharmacological activity while the other is inactive.

Which statement gives correct reasons for this difference?

1 The biological receptors that the drugs bond with are chiral
2 The enantiomers are structural isomers with different chemical properties.
3 The enantiomers have many different physical properties.

A 1,2 and 3 **B** 1 and 2 only **C** 1 only **D** 2 and 3 only

2	**B**	**3**	**B**	**4**	**D**	**5**	**B**
6	**C**	**7**	**D**	**8**	**B**	**9**	**C**

10 **(a)** What is meant by the term 'optical isomerism'?

(b) What conditions must be fulfilled for a compound to exhibit optical activity?

(c) Draw the structural formula of the alkane with the lowest M_r that can exhibit optical isomerism.

Application Questions

11 A hydrocarbon **Q** consists of 86% carbon by mass.

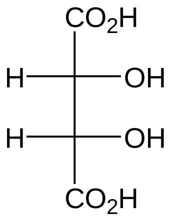
(a) Calculate the empirical formula of **Q**.

(b) 5.0 g of **Q** was found to occupy 2.0 dm^3 at 0 °C and 1 atm. Deduce the molecular formula of **Q**.

(c) **Q** exists as a pair of *cis-trans* isomers. Draw the structural formulae for the isomers.

(d) **P** is a structural isomer of **Q** and does **not** show *cis-trans* isomerism. Suggest a structure for **P**.

12 The effect of plane-polarised light on tartaric acid, $HO_2CCH(OH)CH(OH)CO_2H$, was investigated by Louis Pasteur.



tartaric acid

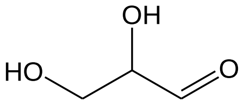
Pasteur identified three different types of tartaric acid molecule.

- molecule **A** rotated plane-polarised light to the right.
- molecule **B** rotated plane-polarised light to the left.
- molecule **C** has no effect on plane-polarised light.

(a) Label each chiral centre in tartaric acid with an asterisk (*).

(b) Suggest an explanation for the observations about molecules **A**, **B** and **C** made by Pasteur.

13 Glyceraldehyde as shown below is chiral and exists as two enantiomers, *D*-glyceraldehyde, and *L*-glyceraldehyde.



glyceraldehyde

(a) Identify the chiral centre using (*).

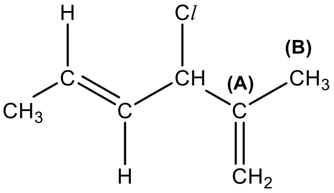
(b) Given that sample I contains only the *D*-isomer which rotates the plane of plane-polarised light in the clockwise direction. Complete the table below using the given information.

sample number	relative amount of *D*-isomer in sample	relative amount of *L*-isomer in sample	about the sample	is sample optically active?	direction of rotation of plane-polarised light
I	100	0	pure *D*-isomer	Yes	clockwise
II	75	25	excess *D*-isomer		
III	50	50			
IV	25	75			
V	0	100			

(c) The samples of glyceraldehyde were analysed for optical activity. Only one sample was found to be optically inactive.

Identify the optically inactive sample and account for its optical activity.

14 Compound **X** can exhibit stereoisomerism.



Compound **X**

(a) State the maximum number of stereoisomers that **X** can have. Explain your answer. [2]

(b) Draw all the stereoisomers of **X**. [4]

(c) Draw a structural isomer of **X** which does **not** exhibit any form of stereoisomerism. [1]

(d) Explain why the C−C bond between carbons **(A)** and **(B)** is stronger than a typical C−C bond in an alkane such as ethane. [2]

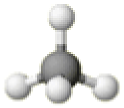
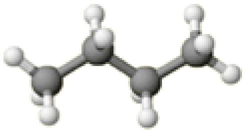
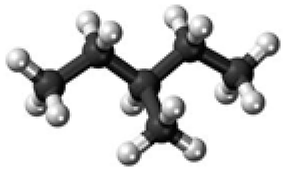
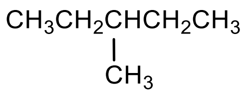
3 HYDROCARBONS - ALKANES AND CYCLOALKANES

3.1 INTRODUCTION

Alkanes are the simplest of the homologous series of organic compounds and are also the least reactive hydrocarbons. Alkanes are **saturated** hydrocarbons as they contain only C–H and C–C **<u>single</u>** (σ) bonds with a maximum of 4 **σ** bonds per carbon. All C atoms in alkanes are **sp^3 hybridised** with each C atom in a **tetrahedral** geometry. Alkanes can be classified as ***acyclic*** (aliphatic, straight and branched chains) or cyclic closed rings.

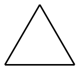
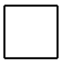
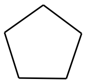
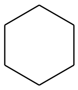
3.1.1 Acyclic (non-cyclic) Alkanes

Acyclic alkanes have the general formula $\mathbf{C_{\mathit{n}}H_{2\mathit{n}+2}}$ and contain zig-zag chains of **C** atoms. Acyclic alkanes can be classified as straight and/or branched chains.

		
methane	butane	3-methylpentane
CH_4	$CH_3CH_2CH_2CH_3$	 $\underset{\displaystyle CH_3}{CH_3CH_2\overset{}{C}HCH_2CH_3}$
Straight chain	Straight chain	Branched chain

3.1.2 Cyclic Alkanes (closed rings alkanes)

Cyclic alkanes (cycloalkanes) have the general formula $\mathbf{C_{\mathit{n}}H_{2\mathit{n}}}$ (same as alkenes).

Molecular formula	Name	Skeletal formula
C_3H_6	cyclopropane	
C_4H_8	cyclobutane	
C_5H_{10}	cyclopentane	
C_6H_{12}	cyclohexane	

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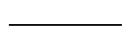
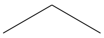
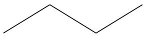
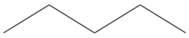
3.2 NOMENCLATURE OF BRANCHED CHAIN ISOMERS (IUPAC SYSTEM)

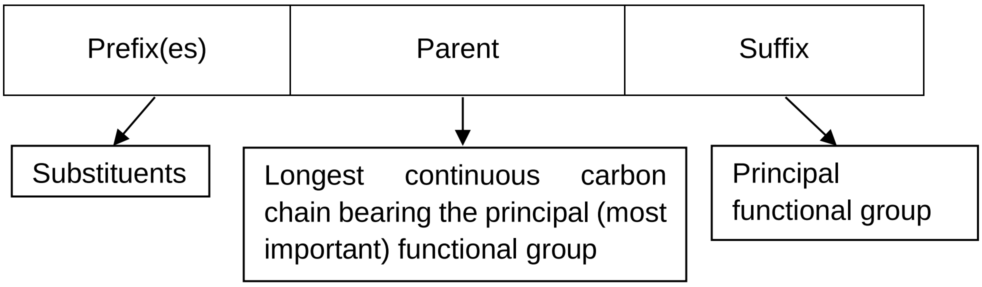
Success criteria:
• I can deduce the structure of an alkane from its given IUPAC name (and vice versa)

The names of alkanes end with the letters '-*ane*'. The following are the names for the first 6 straight-chain alkanes.

n	**Molecular formula**	**Name**	**Condensed Structural formula**	**Skeletal formula**
1	CH_4	meth**ane**	CH_4	
2	C_2H_6	eth**ane**	CH_3CH_3	
3	C_3H_8	prop**ane**	$CH_3CH_2CH_3$	
4	C_4H_{10}	but**ane**	$CH_3(CH_2)_2CH_3$	
5	C_5H_{12}	pent**ane**	$CH_3(CH_2)_3CH_3$	
6	C_6H_{14}	hex**ane**	$CH_3(CH_2)_4CH_3$	

With branching, atoms or groups of atoms that make up the side chains have to be considered a substituent.

The IUPAC name of an organic compound consists of a **parent** (or **stem**), a **suffix** and as many **prefixes** as necessary.



Prefix(es) → Substituents

Parent → Longest continuous carbon chain bearing the principal (most important) functional group

Suffix → Principal functional group

How to name an organic compound

1 Identify the longest continuous carbon chain for the parent name.

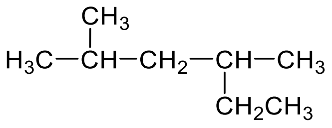
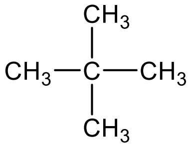
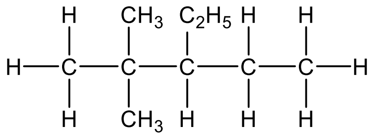
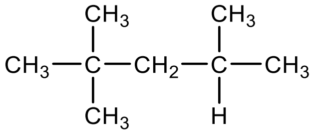
2 Numbers carbon atoms in the longest chain nearer to the first branch point

3 Identify and label numbers on the substituents. If two or more substituents are present, cite them in alphabetical order.

The number prefixes *di*-, *tri*-, *tetra*-, etc. are ignored in alphabetising.

Check-point 1

1 Determine if each alkane is named correctly using IUPAC nomenclature.
If the naming is **incorrect**, give the correct IUPAC name.

Organic compound	Is naming correct? (Y / N)	Correct IUPAC name (if relevant)
 $H_3C-CH(CH_3)-CH_2-CH(CH_2CH_3)-CH_3$ 2-methyl-4-ethylpentane		
 $CH_3-C(CH_3)_2-CH_3$ 2,2-methylpropane		
 $CH_3-C(CH_3)_2-CH(C_2H_5)-CH_2-CH_3$ 4,4-dimethyl-3-ethylpentane		
 $CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$ 2,2,4-trimethylpentane		

2 Draw the skeletal formula of 2-ethyl-1,1-dimethylcyclohexane.

3.3 ISOMERISM

Alkanes with 4 or more carbon atoms exhibit structural isomerism due to branching of the hydrocarbon chains. Optical isomerism can also occur in higher members of the alkane series.

3.4 PHYSICAL PROPERTIES OF ALKANES

Success criteria:
• I can explain the difference in melting point and boiling point between alkanes. • I can understand the solubility of alkanes in different types of solvent.

Alkane molecules are made up of only C and H atoms which have **<u>similar electronegativities</u>**. The C–H bond is considered **non-polar** with a very small dipole moment. Thus, alkane molecules are held together by weak instantaneous dipole-induced dipole interactions.

3.4.1 Boiling and Melting point

Remember?
The strength of instantaneous dipole - induced dipole (id-id) interactions between molecules increases with increasing size of electron cloud.

Molecules of branched alkanes have a smaller surface area of contact between adjacent molecules than that of their straight-chain isomers, resulting in a weaker idid interaction.

The boiling and melting points of alkanes **increase** as the number of carbon atoms in the molecules increases due to the increase in M_r and hence the increasing size of electron cloud.

Formula	**Name**	M_r	**Melting point / °C**	**Boiling point / °C**	**State** (at r.t.p)
CH_4	Methane	16	–182	–162	gas
C_2H_6	Ethane	30	–183	–89	gas
C_3H_8	Propane	44	–188	–42	gas
C_4H_{10}	Butane	58	–138	0	gas
C_5H_{12}	Pentane	72	–130	36	liquid
C_6H_{14}	Hexane	86	–95	69	liquid

Branched-chain alkanes usually have **lower** boiling points than their corresponding straight-chain alkanes. The greater the degree of branching, the lower the boiling point of the compound.

3.4.2 Solubility

For dissolution to take place, solute-solvent interaction should be stronger or comparable to solute-solute and solvent-solvent interaction.

Alkanes are **insoluble** in **polar** solvents (e.g. water) but **soluble** in **non-polar solvents** (e.g. CCl_4, benzene).

3.4.3 Density

Density of alkanes **increases** down the homologous series. M_r is larger and stronger instantaneous dipole-induced dipole interactions between molecules bring the alkane molecules closer to each other. Larger mass and smaller volume results in higher density. However, density of alkanes decreases with more branching in the molecules of similar M_r values due to poorer packing (branched isomers occupy bigger space than straight chain).

3.4.4 Viscosity

Viscosity is a measure of the internal resistance to the flow of a fluid which form friction between neighbouring molecules. The viscosity of liquid alkanes increases with increasing M_r as the strength of intermolecular instantaneous dipole-induced dipole interactions increases.

3.5 CHEMICAL PROPERTIES OF ALKANES

3.5.1 Reactivity

Success criteria:
• I can explain why alkanes are generally unreactive towards most reagents.

Alkanes are generally unreactive and chemically inert towards most chemical reagents such as acids, bases, oxidising and reducing agents.

Alkanes lack chemical reactivities as:
(i) the **C–H** bonds are **non-polar** (C and H have **<u>similar</u> <u>electronegativities</u>**)
(ii) C–C and C–H bonds are rather strong.

As a result, alkane do not have electron rich or electron poor centres to attract reactive charged species. This renders alkanes unreactive towards ionic and polar reagents. Instead, alkanes react with oxygen **(combustion)** and halogens involving electrically neutral free radicals **(substitution)**, the two most important reactions.

3.5.2 Combustion

Success criteria:
• I can write balanced equation for alkanes to undergo combustion. • I can deduce the identity of a hydrocarbon based on combustion data

Alkanes burn *exothermically* in excess oxygen when ignited.

(i) Limited supply of oxygen

Incomplete combustion of alkanes results in the production of CO and/or C (as black soot) and water.

e.g. $2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$
$CH_4 + O_2 \rightarrow C \text{ (soot)} + 2H_2O$

(ii) Excess supply of oxygen

Complete combustion of alkanes results in the production of CO_2 and H_2O as the only products.

e.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -890 \text{ kJ mol}^{-1}$

General equation for the combustion of hydrocarbon:

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

Many alkanes, such as methane (natural gas), propane, butane, are used as fuels due to their ease of burning which are highly exothermic.

Alkanes burn readily in the gaseous state. Hence, solid and liquid alkanes must be vapourised before they will burn. Higher members of alkanes have a lower volatility and burn less readily to give sooty flames.

Check-point 2

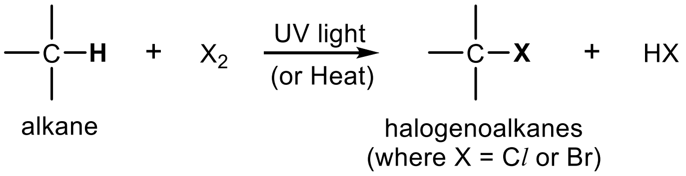
State the oxidation number of carbon in each molecule.

	CO	HCHO	$C_aH_3C_bH_2OH$
oxidation state of C			C_a : C_b :

3.5.3 Free radical substitution

Success criteria:
- I can describe/ outline the free radical substitution (FRS) mechanism with reference to initiation, propagation and termination reactions using equations and curly arrows (1st step only). - I can understand why FRS is an unsuitable method for many organic synthesis. - I can predict the structures of the possible products from FRS. - I can apply my understanding of FRS mechanism to a novel context.

Alkanes react with halogens such as Cl_2(g) or $Br_2(l)$ in the presence of **UV light** or at **high temperatures** to produce halogenoalkanes via **free radical substitution** (involves **free radicals**).



This reaction is called **substitution** as one or more of the **hydrogen atoms** in the alkane are **replaced** (substituted) **by** the **halogen** atoms.

Video on Free Radical Substitution Mechanism

https://tinyurl.com/frsdance

(i) Free-radical substitution mechanism

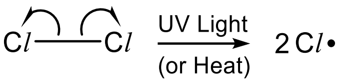
It involves 3 elementary steps:

1 Initiation

2 Propagation

3 termination

Example: chlorination of methane: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Mechanism	Explanation
Initiation  $Cl-Cl \xrightarrow[\text{(or Heat)}]{\text{UV Light}} 2Cl\bullet$	A brief exposure to a high temperature / UV light cleaves $Cl–Cl$ bond **homolytically** to produce low concentration of **free $Cl\bullet$ radicals** (atoms). Each half curly arrow () shows the movement of **one electron**.
Propagation $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + \mathbf{HCl}$ --**(a)** $\bullet CH_3 + Cl_2 \rightarrow Cl\bullet + \mathbf{CH_3Cl}$ --**(b)**	Once $Cl\bullet$ radicals are formed, they go through a **chain reaction** sequence (repeated cycle of steps **(a)** and **(b)**). **$Cl\bullet$** used and regenerated keeps the chain reaction going.
Termination $2Cl\bullet \rightarrow Cl_2$ $\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$ $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$ (any 2 equations)	This step involves **2 reactive free radicals** combining to form a stable (unreactive) product**. Free radicals** are **consumed** but **not generated**. This step occurs towards the end of the reaction where collision between radicals are more likely as effective collision between decreasing number of reactant alkane molecule become increasingly difficult.

Note:
Initiation: Halogen molecule produces low concentration of halogen radicals

Propagation: repeated cycle of one or more pairs of steps **(a)** and **(b)**:
(a) halogen radical produces organic radical. **(b)** regeneration of halogen radical.

Poly substitution occurs through multiple iteration of **(a)**-**(b)** pairs
Mono-substitution: 1 pair
Di-substitution: 2 pairs
Tri-substitution: 3 pairs
Refer to 3.5.3 c.

Important points to note*

a. *Why does the Cl-Cl bond break preferentially during the initiation step?*

From *Data Booklet*:
BE(Cl-Cl) = 244 kJ mol^{-1} BE(C–H) = 410 kJ mol^{-1} BE(C–C) = 350 kJ mol^{-1}

Energy provided by the UV light is only sufficient to overcome weakest Cl–Cl bond but not those of C–H and C–C bonds.

b. *Are H• radicals (atoms) formed during the propagation step? Why?*

No. Consider 2 two possible propagation steps:

$CH_4 + Cl\bullet \rightarrow \bullet CH_3$ (***alkyl radical***) + HCl $\Delta \boldsymbol{H}_{\mathbf{rxn\ 1}}$

$CH_4 + Cl\bullet \rightarrow CH_3Cl + H\bullet$ (***hydrogen radical***) $\Delta \boldsymbol{H}_{\mathbf{rxn\ 2}}$

$\Delta H_{\text{rxn 1}}$ = BE(C–H) – BE(H–Cl) = 410 – 431 = **–21** kJ mol^{-1}

$\Delta H_{\text{rxn 2}}$ = BE(C–H) – BE(C–Cl) = 410 – 340 = **+70** kJ mol^{-1}

Remember?
$\Delta H_{reaction} = \sum BE_{\text{(bonds broken)}} - \sum BE_{\text{(bonds formed)}}$

The above ΔH values show that it is energetically more favorable to form alkyl radicals than hydrogen radicals. Thus, **no H• radicals are formed during propagation**. Hence, hydrogen gas is never formed in such reactions.

c. *Does the propagation reaction stop at monosubstitution?*

No. $CH_3\boldsymbol{Cl}$ formed by monosubstitution can **undergo further substitution** to produce **multi-substituted halogenoalkanes**, $CH_2\boldsymbol{Cl}_2$, $CH\boldsymbol{Cl}_3$ and $C\boldsymbol{Cl}_4$ as shown below.

$$CH_4 + Cl_2 \rightarrow CH_3\boldsymbol{Cl} + CH_2\boldsymbol{Cl}_2 + CH\boldsymbol{Cl}_3 + C\boldsymbol{Cl}_4$$
(*various degree of substitution*)

$Cl\bullet + CH_3Cl \rightarrow \bullet CH_2Cl + HCl$
$\bullet CH_2Cl + Cl_2 \rightarrow Cl\bullet + \boldsymbol{CH_2Cl_2}$ (<u>dichloromethane</u> is produced)

$Cl\bullet + CH_2Cl_2 \rightarrow \bullet CHCl_2 + HCl$
$\bullet CHCl_2 + Cl_2 \rightarrow Cl\bullet + \boldsymbol{CHCl_3}$ (<u>trichloromethane</u> is produced)

$Cl\bullet + CHCl_3 \rightarrow \bullet CCl_3 + HCl$
$\bullet CCl_3 + Cl_2 \rightarrow Cl\bullet + \boldsymbol{CCl_4}$ (<u>tetrachloromethane</u> is produced)

Hence free radical substitution **does not give a single product** but a mixture of products and has limited *synthetic utility* in the laboratory because of the multiplicity of products formed.

d. How to minimise multiple substitutions?

By modifying the conditions of the reaction, it is possible for the reaction to favour formation of one product over others. Product that is formed in a significantly greater quantity is known as the **major product** while those formed in smaller quantities are known as the **minor products**.

When **excess alkane** (or **limited** $\boldsymbol{Cl_2}$) is used, **monosubstituted** alkane, e.g. CH_3Cl, predominates since there is a higher probability for Cl• radicals to collide with

CH_4 molecules instead of CH_3Cl molecule in the propagation step. Thus, a considerable amount of CH_3Cl will be formed.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

When **excess Cl_2** is used, the more **highly substituted** products such as CH_2Cl_2, $CHCl_3$, CCl_4 are formed.

$$CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$$
$$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$$
$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$$

e. What are the conditions for free radical substitution of alkanes with different halogens of different reactivity?

Reactivity of halogens with alkanes **increases** in the order (**reverse** of the X–X bond energies):

$$I_2 < Br_2 < Cl_2 < F_2$$

F_2	:	reaction proceeds explosively even at r.t.p. (not carried out in laboratory)
Cl_2 / Br_2	:	reaction occurs at 250 – 400 °C or in UV light
I_2	:	least reactive and reaction is so slow that it is not carried out

For example:

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ **$\Delta H_{rxn\ 1}$**

$\Delta H_{rxn\ 1}$ = [BE(C–H) + BE(Cl–Cl)] – [BE(C–Cl) + BE(H–Cl)]
= (410 + 242) – (340 + 431) = **–119 kJ mol^{-1}**

$CH_4 + I_2 \rightarrow CH_3I + HI$ **$\Delta H_{rxn\ 2}$**

$\Delta H_{rxn\ 2}$ = [BE(C–H) + BE(I–I)] – [BE(C–I) + BE(H–I)]
= (410 + 151) – (240 + 299) = +**22 kJ mol^{-1}**

As $\Delta H_{rxn\ 2}$ is positive, the reaction is endothermic and it is much less likely to synthesise iodoalkanes by this method.

Check-point 3

1. Write an overall equation for the formation of bromoethane from the reaction of ethane with bromine.

2. Describe the mechanism for the synthesis of bromoethane from ethane.

Name of Mechanism:

Important Note:

When describing/ outlining a reaction mechanism,

- *state name of the mechanism*
- *Label "initiation", "propagation" and "termination" steps and give the structural formula of the organic molecule/ radical for each equation under each step.*
- *draw a half curly arrow to show movement of an electron*
- *show lone electron,* **(•)**, *of all radicals. For alkyl radical, must place the "*•*" next to the C atom. E.g.*

$CH_3CH_2\bullet$ × $CH_3\dot{C}H_2$ √

- *no need for detail descriptions / explanations*

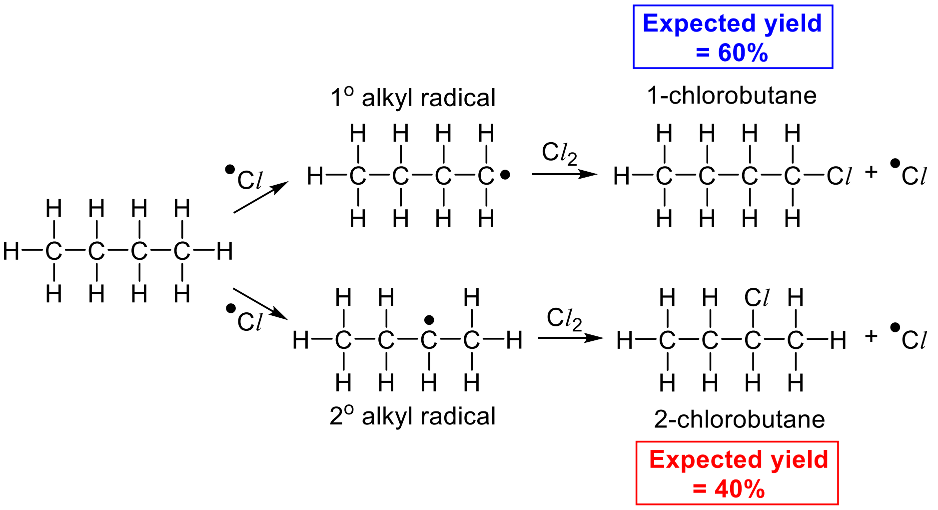
(ii) Expected yield for monosubstitution of alkane (Based on probability)

Success criteria:

- I can use probability to predict the expected/ theoretical relative ratio of different monosubstituted product for an alkane undergoing free radical substitution.

In higher members of alkanes, substitution of hydrogen atoms at different carbon atoms leads to different products.

e.g. Butane reacts with chlorine in the presence of UV light to form two mono-substituted products as shown below.



Expected yield = 60%

Expected yield = 40%

There are a total of 4 H that can be substituted to form 2-chlorobutane while there are a total of 6 H that can be substituted to form 1-chlorobutane.

Assuming each H has an equal chance of being substituted by C*l*, thus molar ratio of 1-chlorobutane and 2-chlorobutane formed is 60% : 40%, i.e. 3 : 2. This is the theoretical ratio.

<u>Check-point 4</u>

1. The following alkanes undergo free radical substitution with chlorine. Identify the monochlorinated products and their expected ratio.

(a) 2-methylpropane

(b) Pentane

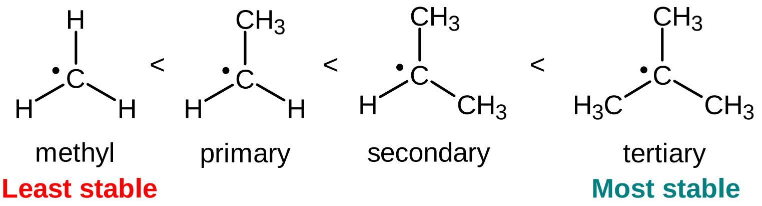
(ii) Rate of substitution at 1^o, 2^o & 3^o carbon atoms

Success criteria:
• I can explain how electron-donating alkyl groups stabilize the alkyl radical, thus favouring substitution at a particular carbon, causing the experimental ratio to differ from theoretical ratio.

Important Note:

Greater stability in the reactive intermediate lowers the activation energy of the reaction.

Radical stability increases in the order
methyl < primary < secondary < tertiary



Alkyl groups are weakly **electron-donating / releasing**. They stabilise alkyl radicals by shifting their electron density towards the electron-deficient carbon atom that bears the lone electron. The **more alkyl groups** bonded to this carbon, the **more stable** the radical due to a decrease in its electron deficiency.

Thus, a tertiary (3°) radical (radical C connected to 3 other alkyl groups) is the most stable of all, followed by the secondary (2°) radical, and in turn, the primary (1°) radical (radical C connected to 1 other alkyl groups).

Check-point 5

Based on the probability consideration, substitution of H atoms of butane would produce 1-chlorobutane and 2-chlorobutane in the expected molar ratio of **60% : 40%**. However, the experimental yields for 1-chlorobutane and 2-chlorobutane are 30% and 70% respectively.

Explain the discrepancy between the expected and experimental ratios of the monochlorinated products.

(**1^o / 2^o**) alkyl radicals are **more** stable than (**1^o / 2^o**) alkyl radicals due to (**more/fewer**) electron donating alkyl groups. (**1^o / 2^o**) alkyl radicals are **formed preferentially**. Hence, forming **more** of 2-chlorobutane than the expected yield of 40%.

3.6 PETROLEUM AND ITS ENVIRONMENTAL CONSEQUENCES

3.6.1 Environmental pollutants

Success criteria:
• I can state the environmental pollutants and the impacts they have on the environment.

During the combustion of petrol, the following pollutants may be produced in the car exhaust emissions:

(i) Smog

As a result of incomplete combustion of fuel, unburnt hydrocarbons that escape into the atmosphere become smog under the strong sunlight and can cause lung damage.

(ii) Carbon monoxide

CO is formed from the incomplete combustion of hydrocarbon fuels.

CO binds much more strongly to haemoglobin than O_2 in red blood cells. This reduces the oxygen-carrying ability of the cells, which can be fatal.

(iii) Nitrogen oxides (NO_x, nitrox)

The combustion of fuel in car engines causes the temperature to rise so high that it can break N≡N bonds in nitrogen, which then react with oxygen to form NO and NO_2. NO and NO_2 (collectively termed **nitrox**, **NO_x**) can contribute to

- formation of smog through reaction with other air pollutants. PAN is a major component of smog which is harmful to plants and humans.

$$\text{Hydrocarbons} + O_2 + NO_2 + \text{light} \rightarrow \text{peroxyacetyl nitrate (PAN)}$$

- formation of ozone at lower atmosphere. **High concentration of ozone at lower atmosphere causes respiratory problems.**

$$NO_2 \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$

Recall homogeneous catalyst from reaction kinetics

- NO_2 acts as a **catalyst for the oxidation** of SO_2 to SO_3.

$$\text{Overall Eqn: } SO_2 + \tfrac{1}{2} O_2 \rightarrow SO_3$$

Mechanism:

$$NO_2 + SO_2 \rightarrow SO_3 + NO$$
$$NO + \tfrac{1}{2} O_2 \rightarrow NO_2 \text{ (regenerated)}$$

SO_3 dissolves in rainwater to cause acid rain (H_2SO_4).

3.6.2 Use of catalytic converter

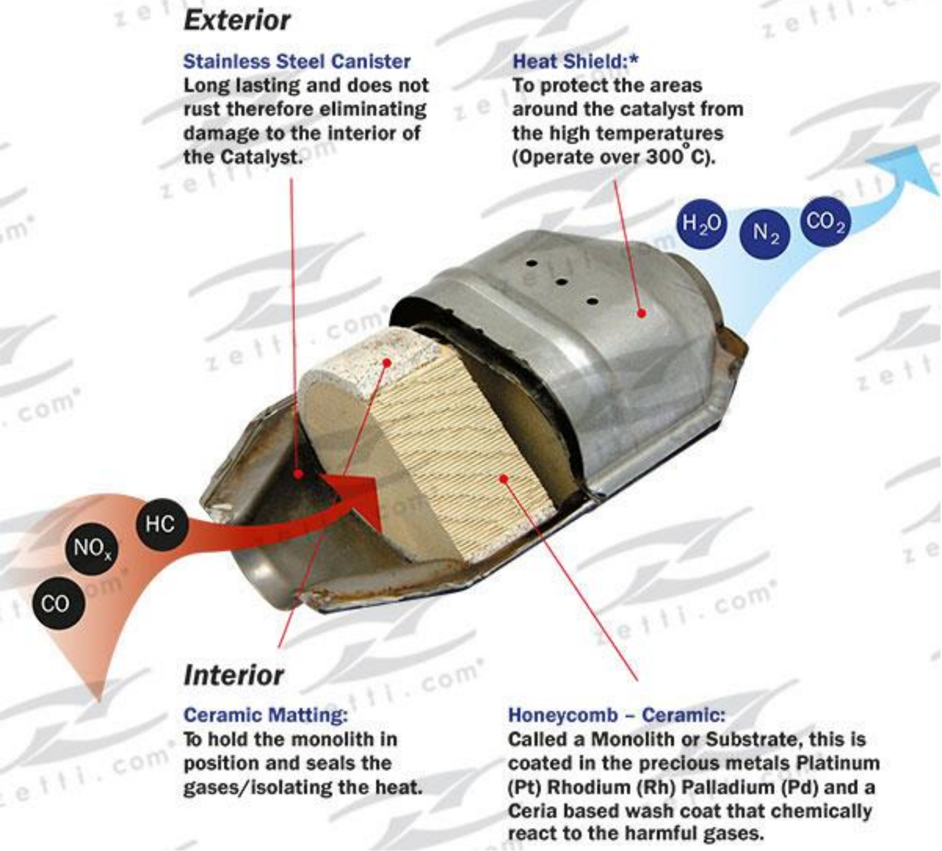
Success criteria:
- I understand the purpose of catalytic converter in motor vehicles. - I understand the reactions in the catalytic converters are redox reactions.

To reduce pollution from motor vehicles, catalyst converters containing rhodium, platinum and/or palladium are fixed onto the exhaust pipes. These catalysts convert the more harmful C, CO, NO, NO_2 and unburnt hydrocarbons to less harmful or harmless compounds of CO_2, H_2O, N_2 and O_2 shown below.

hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen

$2CO + 2NO \rightarrow 2CO_2 + N_2$ (CO is oxidised to CO_2, NO is reduced to N_2)

$2NO_2 + 2C \rightarrow 2CO_2 + N_2$ (C is oxidised to CO_2, NO_2 is reduced to N_2)



3.6.3 Green House Gases and the Enhanced Green House Effect

Many greenhouse gases occur naturally in the atmosphere, such as carbon dioxide, methane (CH_4), water vapor, and nitrous oxide (N_2O). The problem we now face is that human activities – particularly burning fossil fuels (coal, oil and natural gas), agriculture and land clearing – are increasing the concentrations of greenhouse gases.

The disruption to Earth's climate equilibrium caused by the increased concentrations of greenhouse gases has led to an increase in the global average surface temperatures. This process is called the **enhanced greenhouse effect.**

The greenhouse gases that was emitted directly in significant quantities are:

- **Carbon dioxide (CO_2).** Accounts for around 75% of the warming impact of current human greenhouse-gas emissions. The key source of CO_2 is the burning of fossil fuels such as coal, oil and gas, though deforestation is also a very significant contributor.

- **Methane (CH_4).** Accounts for around 14% of the impact of current human greenhouse-gas emissions. Key sources include agriculture (especially livestock and rice fields), fossil fuel extraction and the decay of organic waste in landfill sites.

Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I can deduce the structure of an alkane from its given IUPAC name (and vice versa)	DQ1,2	
2. I can explain the difference in melting point and boiling point between alkanes. 3. I can understand the solubility of alkanes in different types of solvent.	DQ3	
4. I can explain why alkanes are generally unreactive towards most reagents.	DQ7	
5. I can write balanced equation for alkanes to undergo combustion.	DQ4,6	
6. I can deduce the identity of a hydrocarbon based on combustion data.	DQ5	
7. I can describe/ outline the free radical substitution (FRS) mechanism with reference to initiation, propagation and termination reactions using equations and curly arrows (1st step only).	DQ10, DQ15(iii)	
8. I can understand why FRS is an unsuitable method for many organic synthesis.	DQ9	
9. I can predict the structures of the possible products from FRS.	DQ12, DQ15(i)-(ii)	
10. I can apply my understanding of FRS mechanism to a novel context.	DQ16	
11. I can use probability to predict the expected/ theoretical relative ratio of different monosubstituted product for an alkane undergoing free radical substitution.	DQ11,13-14	
12. I can explain how electron-donating alkyl groups stabilize the alkyl radical, thus favouring substitution at a particular carbon, causing the experimental ratio to differ from theoretical ratio.	DQ13	
13. I can state the environmental pollutants and the impacts they have on the environment.	DQ18	
14. I understand the purpose of catalytic converter in motor vehicles. 15. I understand the reactions in the catalytic converters are redox reactions.	DQ17,18(d)	

HYDROCARBONS - ALKANES AND CYCLOALKANES TUTORIAL

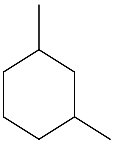
Structure and naming

1 Give the IUPAC name for each compound. Identify any chiral center and draw its stereoisomers, if any.

(a) $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$

(b) $CH_3CH(CH_3)CH(CH_3)CH_2CH_3$

(c)



2 Give the structural formula of the following alkanes.

(a) 4-ethyl-3,4-dimethylheptane

(b) a saturated compound with molecular formula C_5H_{10}

Physical Properties

3 Crude oil consists mainly of alkanes, the saturated hydrocarbons. The alkanes in crude oil can be separated because they have different boiling points.

The table below shows the boiling points of some alkanes.

Alkane	**Boiling point / ^oC**	**M_r**
Butane	0	58
Pentane	36	72
Hexane	69	86
2-methylbutane	28	72
2,2-dimethylpropane	10	72
3-methylpentane	?	86
2,3-dimethylbutane	58	86

(a) State what is meant by the term *saturated hydrocarbon*.

(b) **(i)** Explain the trend in boiling points of the straight chain alkanes.

(ii) Explain the difference in the boiling points of the three isomers with $M_r = 72$.

(iii) With reference to your answer in **b(ii)**, suggest a possible value for the boiling point of 3-methylpentane.

Combustion of hydrocarbon

4 What is the volume of CO_2 formed when y cm^3 of a 50:50 mixture of methane and propane is completely burnt?

A 2y cm^3 **B** $\frac{5y}{2}$ cm^3 **C** 4y cm^3 **D** 5y cm^3

5 When 15 cm^3 of a gaseous hydrocarbon **A** were burned in 100 cm^3 of oxygen, the final gaseous mixture contained 60 cm^3 of carbon dioxide and 10 cm^3 of unreacted oxygen. [All gaseous volumes measured under identical conditions.]

What is the formula of hydrocarbon **A**?

A C_3H_6 **B** C_3H_8 **C** C_4H_8 **D** C_4H_{10}

6 (2016 P3 Q1c) Carbon monoxide is a product of the incomplete combustion of hydrocarbons in internal combustion engines.
Write an equation for the incomplete combustion of octane, C_8H_{18}, giving CO_2 and CO in a 3:1 molar ratio.

Free Radical Substitution

7 (2016 P3 Q4d) Alkanes are very unreactive.

(i) Suggest two reasons why this is the case.

(ii) However, alkanes such as propane, C_3H_8, do react with oxygen and with chlorine.
For each of these reactions,

I. State the conditions under which the reaction is carried out.
II. Name the *type of reaction* which takes place,
III. Write an equation for the reaction.

8 Which explains why chlorine gas reacts readily with ethane in the presence of ultraviolet light?

A UV light breaks the C-H bonds in ethane.

B UV light increases the temperature of the mixture.

C UV light splits the chlorine molecules into chlorine atoms.

D UV light breaks up the chlorine molecules into chloride ions.

9 Which statement best explains why a high yield of 2-bromobutane is **not** usually obtained when butane and bromine react in the presence of UV light?

A Bromine reacts with butane too vigorously.

B Bromine can replace any hydrogen atom in butane.

C The second and third carbon atoms of butane are too strongly electrophilic.

D The second and third carbon atoms of butane are too strongly nucleophilic.

10 Which is a **propagation** step in the reaction between propane and bromine when they are irradiated with ultraviolet light?

A $CH_3CH_2CH_2Br + Br\bullet \rightarrow CH_3CH_2\overset{\bullet}{C}H_2 + Br_2$

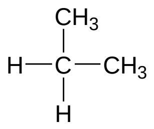
B $CH_3CH_2\overset{\bullet}{C}H_2 + Br\bullet \rightarrow CH_3CH_2CH_2Br$

C $CH_3CH_2\overset{\bullet}{C}HBr + Br_2 \rightarrow CH_3CH_2CHBr_2 + Br\bullet$

D $CH_3CH_2\overset{\bullet}{C}H_2 + Br_2 \rightarrow CH_3CH_2CHBr + HBr$

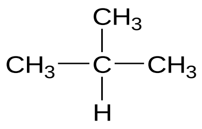
11 An alkane **J** reacts with chlorine gas under ultraviolet light to form only two monochlorinated alkanes in an approximate molar ratio of 6 : 1.
Which could be **J**?

A



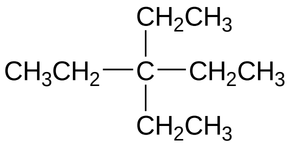
$H-\underset{H}{\overset{CH_3}{C}}-CH_3$

B



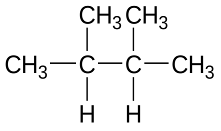
$CH_3-\underset{H}{\overset{CH_3}{C}}-CH_3$

C



$CH_3CH_2-\underset{CH_2CH_3}{\overset{CH_2CH_3}{C}}-CH_2CH_3$

D



$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{C}}-CH_3$

12 Propane reacts with chlorine gas in the presence of UV light.
Which is true about the reaction?

A The maximum number of mono-chlorinated structural isomers with formula C_3H_7Cl is 2.

B C_6H_{12} is present in a small quantity in the product.

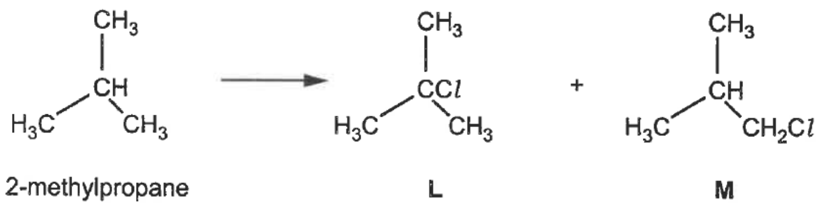
C Homolytic fission occurs only in the initiation step.

D HCl is formed in the termination step.

13 It is found by experiment that during free radical substitution, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

reaction	relative rate
$RCH_3 \longrightarrow RCH_2Cl$	1
$R_2CH_2 \longrightarrow R_2CHCl$	7
$R_3CH \longrightarrow R_3CCl$	21

Predict the relative ratio of the two possible products L and M from the chlorination of 2-methylpropane, using the information in the table above, together with the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule.
Explain your answer.



Application Questions

14 **A** and **B** are two structural isomers with the molecular formula C_4H_{10}.
When **A** reacts with chlorine gas in the presence of UV light, two monochlorinated alkanes **C** and **D** are formed. Only **D** contains a chiral carbon.
When **B** reacts with chlorine gas in the presence of UV light, two monochlorinated alkanes **E** and **F** are formed.

(a) Identify **A**, **B**, **C**, **D**, **E** and **F** by drawing their structural formulae.

(b) **(i)** State the type of isomerism exhibited by **A** and **B**.

(ii) State the type of isomerism exhibited by **C** and **D**.

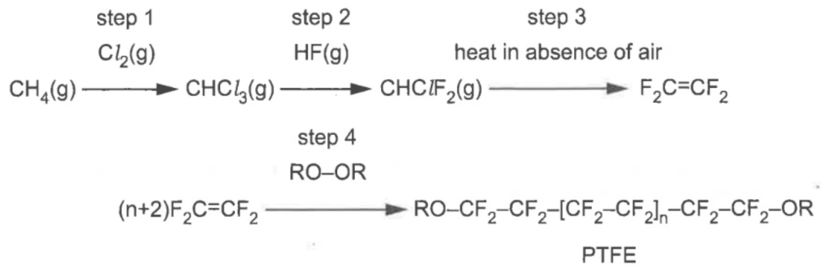
15 In an experiment, propane is added to liquid bromine in the dark. When the reaction mixture is exposed to sunlight, the reddish brown colour slowly disappears and a misty gas is given off.

(i) Identify the misty gas formed in the reaction.

(ii) Write an overall equation for the reaction of one mole of propane, C_3H_8, with two moles of bromine. Draw the structural formulae of all the possible products formed.

(iii) Outline the mechanism for the formation of 1,2-dibromopropane in **b(ii)**.
There are four steps in the propagation stage of the mechanism.

16 (2021 P2 Q4d) The term 'polymer' is given to a large molecule made up of many repeat units.
Poly(tetrafluoroethane), PTFE, is a polymer made from many tetrafluorethane molecules, $F_2C{=}CF_2$.
PTFE can be manufactured from methane in a series of steps.



Step 4 occurs via four separate reactions, **A** to **D**.

A Homolytic fission of RO−OR at 330K and 10-20 atm to produce two RO• radicals

B RO• reacts with one $F_2C{=}CF_2$ molecule to produce a new radical

C Repeated steps involving production of a series to produce

$$RO{-}CF_2{-}CF_2{-}[CF_2{-}CF_2]_n{-}CF_2{-}CF_2\bullet$$

D Two radicals combine to form $RO{-}CF_2{-}CF_2{-}[CF_2{-}CF_2]_{(2n+2)}{-}CF_2{-}CF_2{-}OR$

(i) Explain what is meant by the term homolytic fission.

(ii) Name reactions **A** to **D**.

(iii) Suggest a name for the overall mechanism of step 4.

(iv) Suggest the mechanism which occur in reactions **A** and **B** of step 4. Use curly arrows to show movements of electrons.

Petroleum and its environmental consequences

17 (2020 P1 Q20) Exhaust fumes from car engines contain the gases carbon dioxide, nitrogen oxides and unburnt hydrocarbons.

Use of a catalytic converter in the car exhaust changes the gases emitted.

Which statements are correct about the reactions occurring in the catalytic converter?

1. Carbon dioxide is removed by reduction.
2. Oxides of nitrogen are removed by reduction.
3. Unburnt hydrocarbons are removed by oxidation.

A 1 and 3 **B** 2 and 3 **C** 1 only **D** 2 only

18 Car exhausts contain a range of toxic substances that can have a serious impact on health. Once released into the air, these substances are breathed in and transported in the blood stream to all the body's major organs.

A typical composition of gases in petrol engine exhaust fumes is as follows.

Substance	**%**
Water vapour	9
Carbon dioxide	8
Carbon monoxide	4-6
Oxygen	4
Hydrocarbons	0.2
Oxides of nitrogen	0.3

(a) Which gases of exhaust fumes are consequences of incomplete combustion?

(b) Suggest a reason why the exhaust gases contain products of incomplete combustion.

(c) Name a pollutant in the exhaust fumes that has an adverse effect on human health and explain its impact on human health.

(d) Suggest one substance in the exhaust fumes which can convert one of the pollutants into a harmless product in a car fitted with a catalytic converter. Write a chemical equation to support your suggestion.

Ans Key for MCQ:

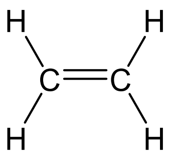
4) A	5) C	8) C	9) B	10) C	11) D	12) A	17) B

4 ALKENES

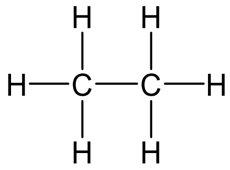
4.1 INTRODUCTION

Alkenes form a homologous series of aliphatic hydrocarbons with the **carbon-carbon double bond** as the distinguishing feature. Alkenes with one C=C bond present in the structure have the general formula, C_nH_{2n}.

Because of its carbon-carbon double bond, an alkene is thus referred to as an **unsaturated hydrocarbon**.



Ethene (C_2H_4)
(presence of C=C) – *unsaturated*)



Ethane (C_2H_6)
(all C-C single bonds – *saturated*)

4.1.1 Nomenclature of Alkenes

Success criteria:
I can deduce the structure of an alkene from its given IUPAC name (and vice versa).

Every name of organic compounds consists of
Prefix — Parent — Suffix

Alkenes have the suffix ***–ene*** to **identify the C=C bond** functional group present in them. When the alkene contains two or three C=C double bonds, it is known as ***di-ene*** and ***tri-ene*** respectively.

- Number the chain from the end closest to the double bonds.
- Lowest number assigned to C=C when it is part of **cyclic ring**.

Cis-trans isomers of alkenes to be distinguished by using the prefix *cis-* or *trans-*.

Checkpoint 1

Give the structural formulae for the following compounds:

(a)	**(b)**
trans-pent-2-ene	2-chloro-3-methylpenta-1,4-diene

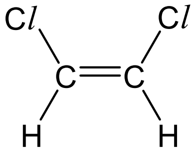
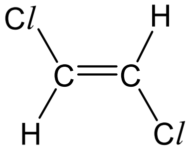
4.2 PHYSICAL PROPERTIES OF ALKENES

Success criteria:
• I can explain the difference in boiling point and melting point between cis and trans isomers.

Similar to alkanes

- Insoluble in water and soluble in non-polar (organic) solvents
- Less dense than water
- Boiling point increases with increasing carbon number
- Branching lowers boiling point

Comparing *cis*- vs *trans*- isomers of 1,2-dichloroethene

	cis-1,2-dichloroethene	*trans*-1,2-dichloroethene
Structural formula		
Boiling point / °C	60.3	47.5
Melting point / °C	–81	–49

Explanation of the difference in boiling points between cis-1,2-dichloroethene and trans-1,2-dichloroethene:

Cis-1,2-dichloroethene molecules are polar and has permanent dipole-permanent dipole attractions between the molecules which is stronger than instantaneous dipole-induced dipole attractions between trans-1,2-dichloroethene molecules. Stronger intermolecular forces require more energy to overcome.

Explanation of the difference in melting points between cis-1,2-dichloroethene and trans-1,2-dichloroethene:

Trans-isomers **pack better** into a *crystal lattice*, leading to more intermolecular forces per unit volume. They generally will have higher melting points than their respective *cis*-isomers.

FYI:
Crystal lattice: the 3D structural arrangement of atoms, ions or molecules in a crystalline material

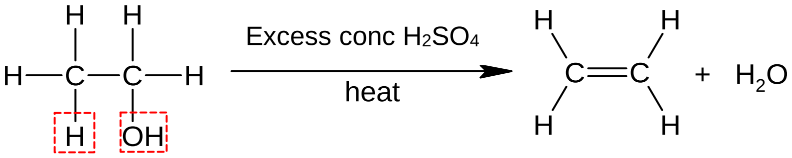
4.3 PREPARATION OF ALKENES

Success criteria:

- I can state the reagents and conditions to convert
  ○ alcohol to alkene
  ○ halogenoalkane to alkene
- I recognize that elimination of H−X from halogenoalkanes and H−OH from alcohol is only possible between two adjacent carbon atoms.
- I can give the structure of the alkene formed from the elimination reaction.

4.3.1 Elimination Reactions

(i) Elimination of H and OH from alcohols

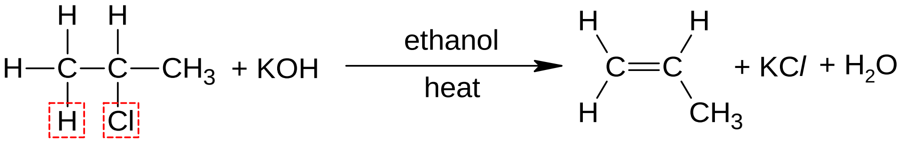


Type of reaction	Elimination
Reagent and condition	Excess concentrated H_2SO_4, heat OR Al_2O_3(s), heat

(ii) Elimination of H and X from halogenoalkanes

Note: Elimination reaction will cause the degree of unsaturation (no. of π bond) in the product to increase by 1

Note: HC*l* eliminated undergoes acid-base reaction with KOH to form KC*l* and H_2O



Type of reaction	Elimination
Reagent and condition	ethanolic KOH/NaOH, heat

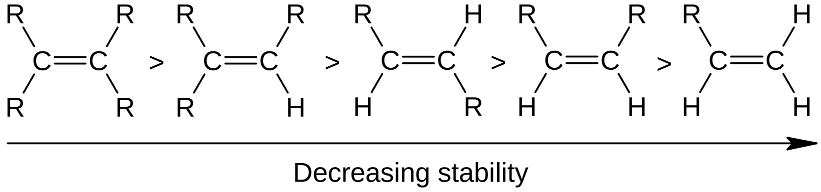
NOTE:

When group of atoms such as H & C*l* or H & OH are **eliminated** from **different pairs of adjacent carbons**, a mixture of alkene isomers is produced, the relative proportion of each alkene will depend on ***Zaitsev's Rule.***

Explanation:
Btw *cis*- and *trans*-alkenes, bulky groups like alkyl groups are best placed far apart from each other to reduce steric strain. Thus, the *trans*-isomer is more

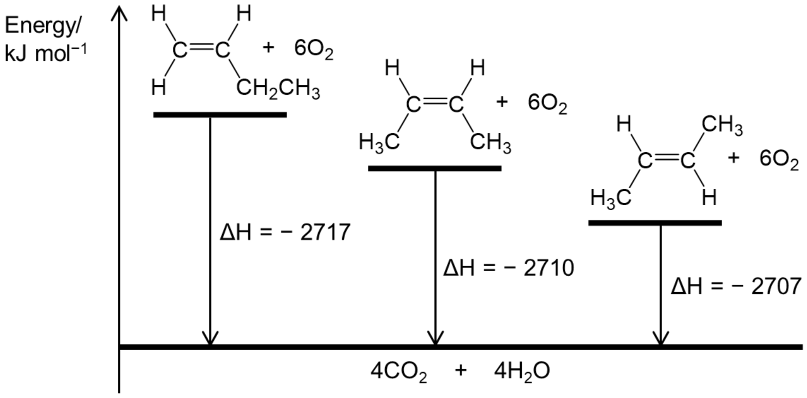
Zaitsev's Rule **(for your info)**
The more highly substituted alkenes are more stable and hence more readily formed in an elimination reaction.

stable and formed in greater quantity.



Experimental Evidence (For your info)

The relative chemical stability of the isomers of an alkene can be easily measured by determining their heats of combustion.



The exothermic combustion reaction converts **isomers of butene** to **same set of oxidised products**; carbon dioxide and water.

Differences in chemical stabilities of the isomers of butene result in different amounts of energy released during combustion. The more stable the isomer, the less exothermic is its combustion reaction.

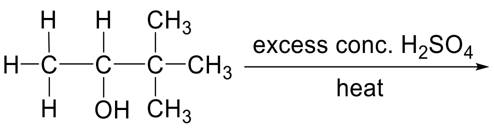
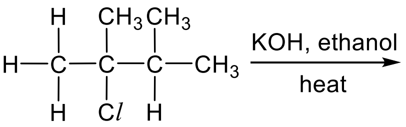
Checkpoint 2

Consider the following molecules. Give the structures of the possible products formed when each undergoes elimination.

Identify the major product, where applicable.

Note: KOH is a base which reacts away the acidic HC*l* molecule from the Halogenoalkane.

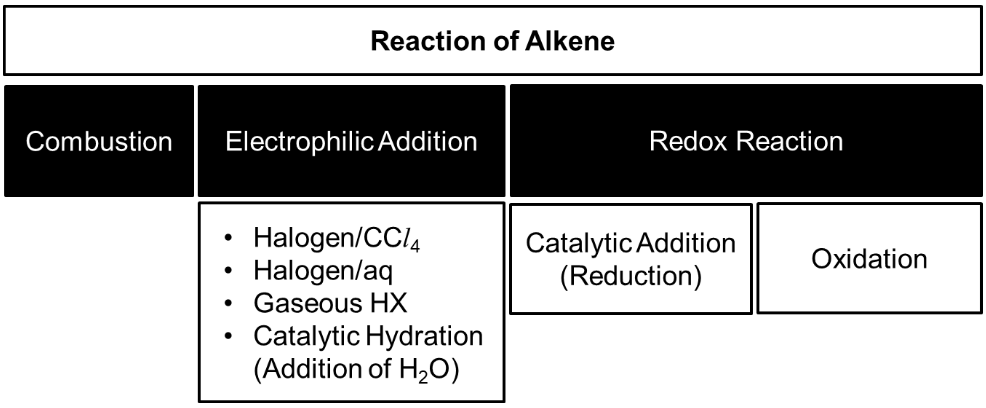
Conc H_2SO_4 is a dehydrating agent which can react H_2O away from the alcohol molecule.

(a)	
(b)	

4.4 REACTIONS OF ALKENES

Success criteria:

- I can state the reagents and conditions for the reactions of alkenes.
- I can deduce the structure of alkenes when the organic products and reagents and conditions are given.
- I can write balanced equations for the reactions.

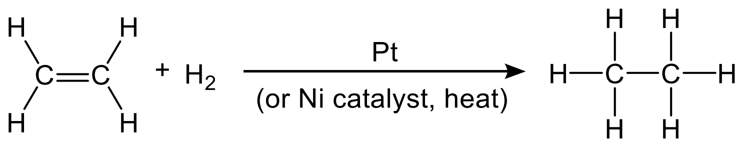


4.4.1 Combustion

Alkenes, being hydrocarbons, undergo complete combustion in excess oxygen to form carbon dioxide and water.

$$C_2H_4\ (g) + 3\ O_2\ (g) \longrightarrow 2\ CO_2\ (g) + 2\ H_2O\ (l)$$

4.4.2 Reduction with hydrogen to form alkane



Type of reaction	Reduction
Reagent and condition	H_2(g), Pt(s) catalyst or H_2(g), Ni(s) catalyst, heat

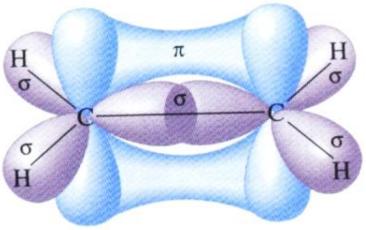
4.4.3 Electrophilic Addition Reactions

Success criteria:
• I can explain why alkenes are reactive towards electrophiles. • I understand why alkenes tend to undergo addition reactions.

(i) Reactivity of Alkene

The C=C bond in alkenes is made up of <u>one σ and one π bond</u>.

- **Sigma bond:** head-on overlap between two $2sp^2$ hybrid orbitals
- **Pi bond:** side-way overlap between two unhybridised 2p orbital



The structure of C=C results in the following reactivity:

- <u>Susceptible to Reactions with Electrophiles</u>

The π electrons are found in the regions above and below the plane of the molecule. Being less tightly bound to the carbon nuclei, the presence of **π electrons causes a region of relatively high electron density at C=C**, thus alkene is more likely to **react with electrophiles** such as HBr and Br_2 molecules.

- <u>Tendency to Undergo Addition Reactions</u>

Recall:
C=C bond consist of a sigma bond (formed via head on overlap of hybrid orbitals) and **π bond** (formed via side-way overlap of unhybridised orbitals).

In addition, **less energy** is required to **break** the **π bond** in the C=C bond as the side-way overlap of atomic orbitals is less effective than head-on overlap ones.

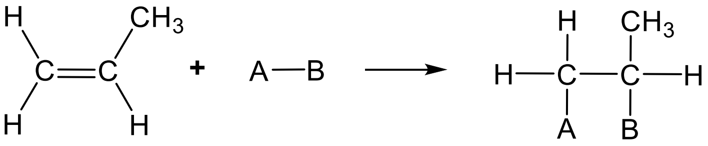
Type of Bond	C—C (σ)	C=C (σ + π)	C—C (π)
Bond Energy/ kJ mol^{-1}	350	610	260

Hence, **alkenes** tend to undergo reactions that **involve** the **breaking** of the weaker **π bond** in the C=C bond, leaving the σ bond intact.

Note:
How to tell if a reaction is an addition reaction?

One clue is the reaction between 2 reactants (one unsaturated) to form 1 product.
2 Reactants → 1 Product

The π electrons are used to form two new σ bonds with the electrophiles to form **one product**.



This reaction is called **<u>electrophilic addition</u>**.

(ii) General Mechanism of Electrophilic Addition

Success criteria:
• I can describe the electrophilic addition mechanism for alkenes using equations, curly arrows and charge when relevant. • I can deduce the structure of the major product from electrophilic addition of an alkene in a *polar* solvent. • I can describe the use of bromine to test for the presence of C=C functional group.

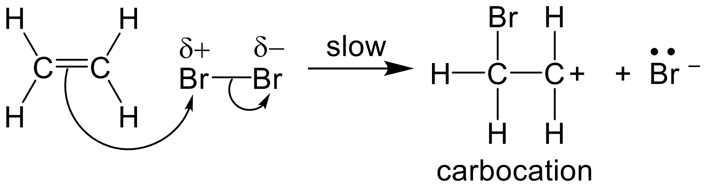
Alkenes tend to undergo **electrophilic addition** reactions.

Important Note:

- (i) State the name of mechanism
- (ii) Show separation of charges (δ+/δ−) on electrophile and charges on ions
- (iii) Between 2 species: Arrows ALWAYS flow from ***electron rich region (π bond of C=C or lone pair of nucleophiles***) to electron deficient region (electrophile or carbocation) Bond breaking within a molecule will be from bond pair to δ− atom.
- (iv) Indicate the slow step

***Name of Mechanism*: Electrophilic Addition**

Step 1:



The loosely bound π electrons of the C=C bond is a region of high electron density.

As the bromine molecule approaches the ethene molecule, the <u>π electron cloud of the C=C induces a dipole in the bromine molecule</u> where a bromine atom attains a partial positive charge and <u>react with ethene as an electrophile</u> in the slow step.

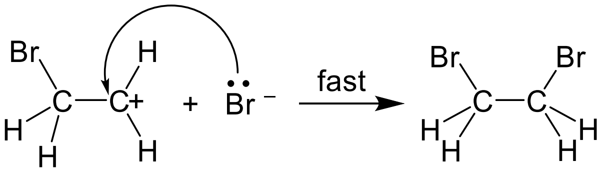
The Br–Br bond undergoes **heterolytic** fission producing a <u>reactive carbocation intermediate</u> and a bromide ion.

Ponder…

1. Carbocation is a reactive intermediate due to its instability Suggest why.

2. What can the carbocation react with to form a stable product based on the "principle of opposite charges attract"?

Step 2:



The negatively charged bromide ion acts as a nucleophile and attacks the unstable positively charge carbocation, forming 1,2-dibromoethane.

(iii) Important Electrophilic Addition Reactions

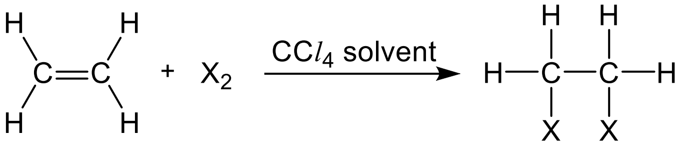
- **Electrophilic Addition of Halogen**

Electrophilic addition with halogen (Br and C*l*) proceeds as per the general mechanism stated in **4.4.3(ii)**. However, solvents that are nucleophilic in nature (e.g. H_2O) may be involved in the fast step producing a mixture of products.

Note:
The rapid and obvious **decolourisation of Br_2** in the above two reactions **(a) and (b)** makes them useful laboratory tests for the presence of unsaturation (presence of C=C double bonds) in organic compounds.

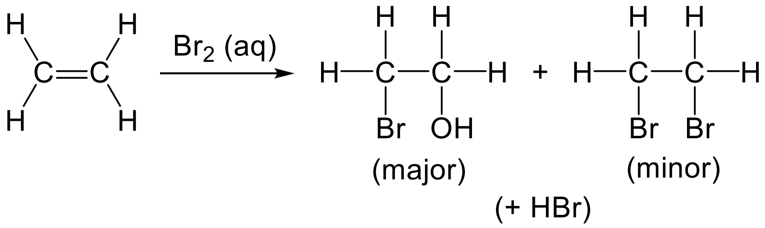
The colours of Br_2 in different medium can be found in the *Data Booklet*. (One page before the Periodic Table)

(a) Halogen dissolved in CC*l*$_4$ (an inert solvent)
(solvent DOES NOT participate in reaction)



Type of reaction	Electrophilic Addition
Reagent and condition	X_2 dissolved in CC*l*$_4$ solvent [X = Br or C*l*]
Observation	Orange-red Br_2 decolourised

(b) AQUEOUS Bromine (bromine water)
(solvent CAN participate in reaction)



Video on Br_2(aq) with alkene

https://tinyurl.com/bfnpxz9p

Type of reaction	Electrophilic Addition
Reagent and condition	Br_2(aq)
Observation	Orange Br_2 decolourised

Important points to note:

1. Why do both products have at least one Br attached?

In the 1st step, Br_2 is the only electrophile to react with ethene, hence the first σ bond formed will be with a Br atom.

2. Why are there two products formed?

In the 2nd step, solvent H_2O can also act as a nucleophile to react with the reactive carbocation forming bromoethanol.

Checkpoint 3

Using suitable curly arrows, complete the mechanism shown below to explain the formation of major and minor products when ethene reacts with aqueous bromine shown in **4.4.3(iii)(b)**.

Important Note:

(i) State the name of mechanism

(ii) Show separation of charges (δ+/δ−) on electrophile and charges on ions

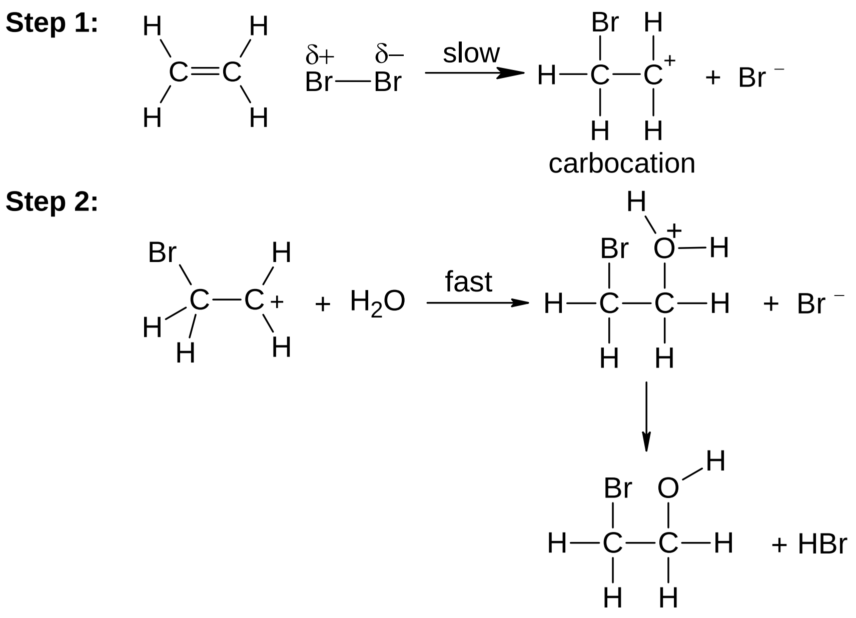
(iii) Between 2 species: Arrows ALWAYS flow from ***electron rich region (π bond of C=C or lone pair of nucleophiles***) to electron deficient region (electrophile or carbocation)

(iv) Bond breaking within a molecule will be from bond pair to δ− atom.

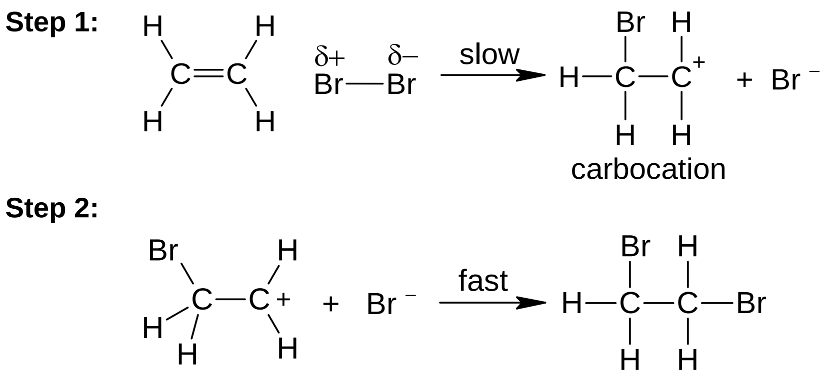
(v) Indicate the slow step

Mechanism:

Formation of MAJOR Product



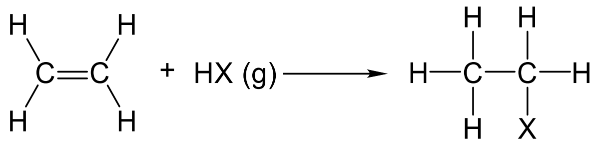
Formation of MINOR Product



3. Why do you think the carbocation is more likely to react with H_2O: than :Br^- to form the addition product?

The solvent H_2O is present in excess, hence it is more abundant as a nucleophile to react with the reactive carbocation.

- **Electrophilic Addition of Hydrogen Halides**



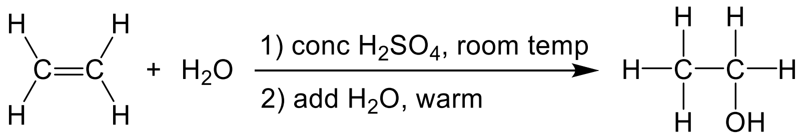
[X = Br or C*l* or I]

Type of reaction	Electrophilic Addition
Reagent and condition	Gaseous HX [X = Br or C*l* or I]

- **Catalytic hydration (Electrophilic Addition of H_2O)**

Since H_2SO_4 is a stronger acid than water, H_2O, it will be the source of H^+ (electrophile).

The H_2O: will then behave as a nucleophile and react with the carbocation.



Type of reaction	Electrophilic Addition
Reagent and condition	1) Conc. H_2SO_4 at room temperature 2) Add H_2O (l) and warm

The above reaction can also be carried out under <u>industrial conditions</u>.

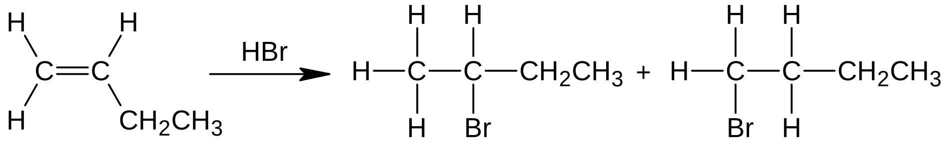
Reagent and condition	H_2O(g), conc. H_3PO_4 catalyst, heat, high pressure

Success criteria:

- I can predict the major product from electrophilic addition of an *asymmetric* alkene.
- I can explain how the major product is formed by considering the stability of carbocation.
- I can understand why the product of electrophilic addition of alkene is optically inactive even if it contains a chiral carbon.

For electrophilic addition across asymmetrical alkenes, **Markovnikov's rule** is used to **predict** the major product formed.

Example: The reaction between hydrogen bromide and but-1-ene will yield two different isomeric products:

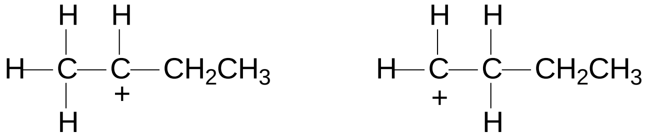


asymmetrical alkene 2-bromobutane (major) 1-bromobutane (minor)

NOTE:
When the atoms that react as the electrophile and nucleophile are different, electrophilic addition of an **asymmetrical alkene** will **yield a mixture of products,** with the major product predicted by **Markovnikov's rule**.

Why is 2-bromobutane the major product?

The C+ in the 2^{o} carbocation stabilized to a larger extent due to 2 electron-donating alkyl groups. This more stable 2° carbocation is formed more abundantly in the rate-determining step, leading to a higher yield of the product.



2^{o} carbocation 1^{o} carbocation

Video on Markovnikov's Rule
Time: 0:30 – 2:38

https://tinyurl.com/dukz7n43

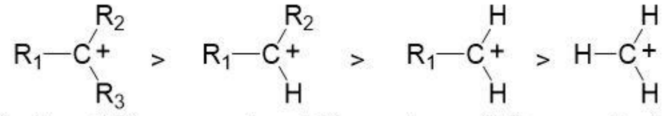
Markovnikov's rule was formulated by Russian chemist Vladimir Vasil'evich Markovnikov in 1870.

The **chemistry principle** behind Markovnikov's Rule is the **formation of the most stable carbocation** in the slow step. The reaction of an electrophile to one carbon atom in C=C creates a positive charge on the adjacent carbon, forming a reactive carbocation intermediate. The more substituted carbocation is formed at a faster rate (lower activation energy due to its greater stability). It will then react with the nucleophile to form the major product.

Explanation of Major product (Important)

Carbocations are generally unstable. The carbocation with more alkyl substituents is more stable as the alkyl groups are **electron donating** and will **reduce the electron deficiency on the carbocation to stabilize it**. The **more stable carbocation is preferentially formed and thus** forms **the major product.**

Therefore, the stability of the carbocations decreases in the following order:



tertiary (3^{o}) secondary (2^{o}) primary (1^{o}) methyl

Important Note:

(i) State the name of mechanism

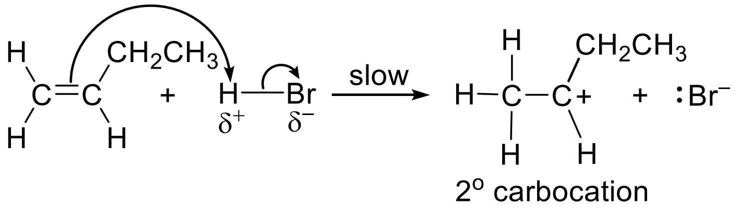
(ii) Show separation of charges (δ+/δ−) on electrophile and charges on ions

(iii) Arrows ALWAYS flow from ***electron rich region (π bond of C=C or lone pair of nucleophiles***) to electron deficient region (electrophile or carbocation)

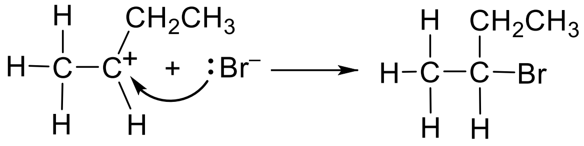
(iv) Indicate the slow step

Formation of Major Product:

Step 1:

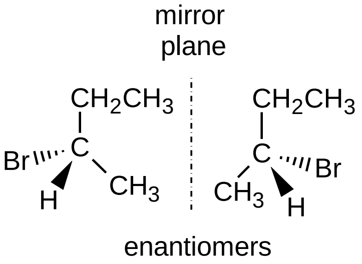


Step 2:



Note:

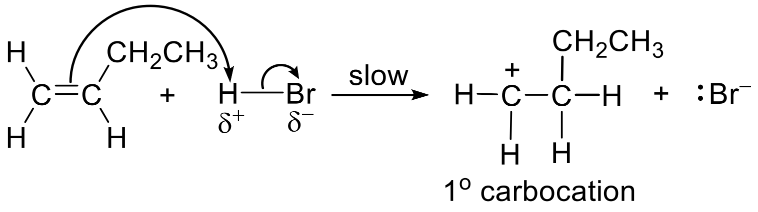
Even though the product molecule contains a chiral carbon, it is a mixture containing equal amount of the 2 enantiomers of 2-bromobutane (a racemic mixture). The product mixture is optically inactive.



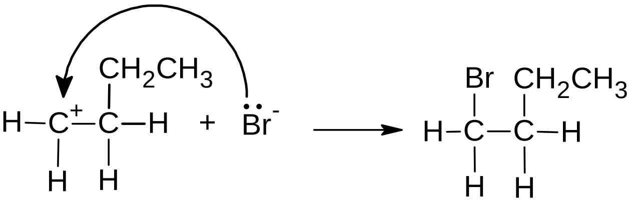
In **Step 2** of the mechanism, Br^- has equal likelihood to attack the trigonal planar carbocation from either side of the plane, thus the 2 enantiomers are formed in equal proportion. The equal but opposite rotation of plane-polarised light by each enantiomer results in net zero optical activity.

Formation of Minor Product:

Step 1:



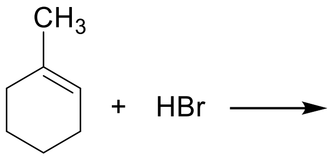
Step 2:

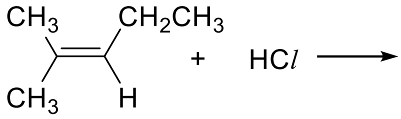


The 2° carbocation, being more stable, is formed more easily. 2-bromobutane is thus formed at higher yield.

Checkpoint 4

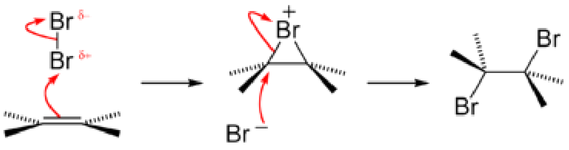
Predict and name the major product of the following reaction:





Electrophilic addition of bromine: The bromonium ion (For your info)
(https://en.wikipedia.org/wiki/Halogen_addition_reaction)

In 1937, Irving Roberts and George E. Kimball first proposed that a cyclic three-membered bromonium ion was formed as an intermediate during the electrophilic addition of Br_2 to an alkenic double bond, to account for the stereoselective *trans*-addition of the two Br atoms.



The reaction mechanism for an alkene bromination can be described as above. In the first step of the reaction, a bromine molecule approaches the electron-rich alkene carbon–carbon double bond. The bromine atom closer to the bond takes on a partial positive charge as its electrons are repelled by the electrons of the double bond.

The atom is electrophilic at this time and is attacked by the pi electrons of the alkene. Due to the large size of bromine, the bromide ion is capable of interacting with both carbons, making a three-membered ring. The bromide ion acquires a positive formal charge and this is known as the "bromonium ion".

When the first bromine atom attacks the carbon–carbon π-bond, it leaves behind one of its electrons with the other bromine that it was bonded to in Br_2. That other atom is now a negative bromide anion and is attracted to the slight positive charge on the carbon atoms. Due to steric repulsion, it can only attack from the other side and forms a bond with one of the carbons. The bond between the first bromine atom and the other carbon atoms breaks, leaving each carbon atom with a halogen substituent.

In this way the two halogens add in an "anti" addition manner, and when the alkene is part of a cycle the dibromide adopts the trans configuration.

4.4.4 Oxidation

Success criteria:
- I can give the structure of products formed when alkene reacts with $KMnO_4$ under different conditions. - I can give the observation when an alkene reacts with $KMnO_4$ in alkaline or acidic medium. - I can deduce the structure of the original alkene from the structure of the oxidised fragments of vigorous oxidation reaction.

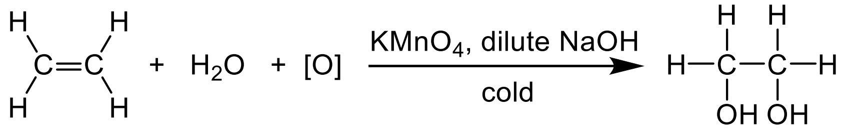
Oxidation of alkenes is a great way to introduce oxygen atom(s) into organic compounds through the formation of carbon−oxygen bonds.

Vigorous and mild oxidation of C=C

The oxidation of carbon-carbon double bonds by the manganate(VII) ion is a well-known reaction in organic chemistry.

(i) Mild Oxidation – formation of diols (two alcohol groups)

The π bond in C=C bond is broken by $KMnO_4$ **at a low temperature and alkaline medium**.



Recall:
[O] and H_2O is used to balance the oxidation reaction with $KMnO_4$

Type of reaction	Mild oxidation
Reagent and condition	$KMnO_4$, NaOH(aq), cold
Observation	Decolourisation of purple $KMnO_4$, brown ppt of MnO_2 formed

This reaction is a useful **distinguishing test** for an alkene from other functional groups.

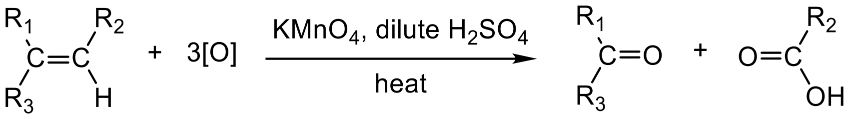
Note: In alkaline medium, purple MnO_4^- is reduced to brown ppt MnO_2

(ii) Vigorous Oxidation

Both the σ AND π bonds in C=C is cleaved by hot acidified $KMnO_4$ and produces two fragments.

This process is known as **oxidative cleavage**.

Note:
[O] is used to balance the oxidation reaction with $KMnO_4$

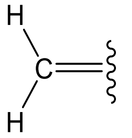
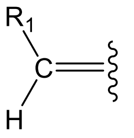
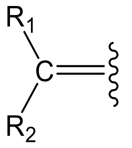
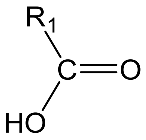
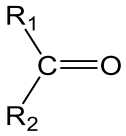


Type of reaction	Vigorous oxidation
Reagent and condition	$KMnO_4$, H_2SO_4(aq), heat
Observation	Decolourisation of purple $KMnO_4$

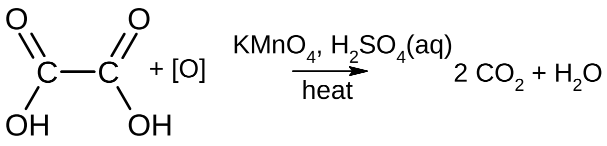
Note: In acidic medium, purple MnO_4^- is reduced to colourless Mn^{2+}.

The **types of product** obtained for vigorous oxidation of alkenes depends on the **number of hydrogen atoms** attached to the C atom of the C=C double bond.

Note:
Oxidation of CH_2= fragment produces H_2CO_3 which decomposes to give CO_2 and H_2O

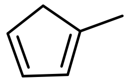
	No. of hydrogen atoms on C=	**2**	**1**	**0**
	Structure	 terminal alkene		
Hot Acidic $KMnO_4$	Observations	• Effervescence due to CO_2(g) formed; • Decolourisation of purple $KMnO_4$	• Decolourisation of purple $KMnO_4$	
	Products after oxidation with hot acidic $KMnO_4$	CO_2 and H_2O	 Carboxylic acid	 Ketone

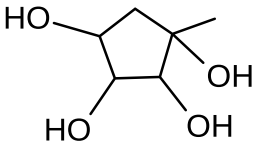
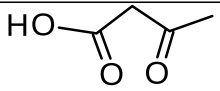
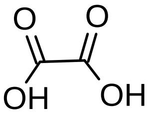
NOTE: Oxidative cleavage of large alkene with multiple C=C bonds may produce ethanedioic acid (HOOC-COOH) as a product. Ethanedioic acid is further oxidised by hot acidified $KMnO_4$ to give CO_2 and H_2O.



Worked Example 1

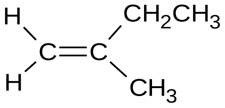
Identify the products when the following compound reacts with $KMnO_4$ under different conditions.



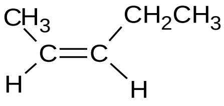
$KMnO_4$, dil NaOH, cold (mild oxidation, breaks π bond ONLY)	
$KMnO_4$, dil H_2SO_4, heat (vigorous oxidation, breaks BOTH σ AND π bonds)	 + 2 CO_2 + H_2O **Note:**  produced undergoes further oxidation by hot acidified $KMnO_4$ to give CO_2 and H_2O

<u>Checkpoint 5</u>

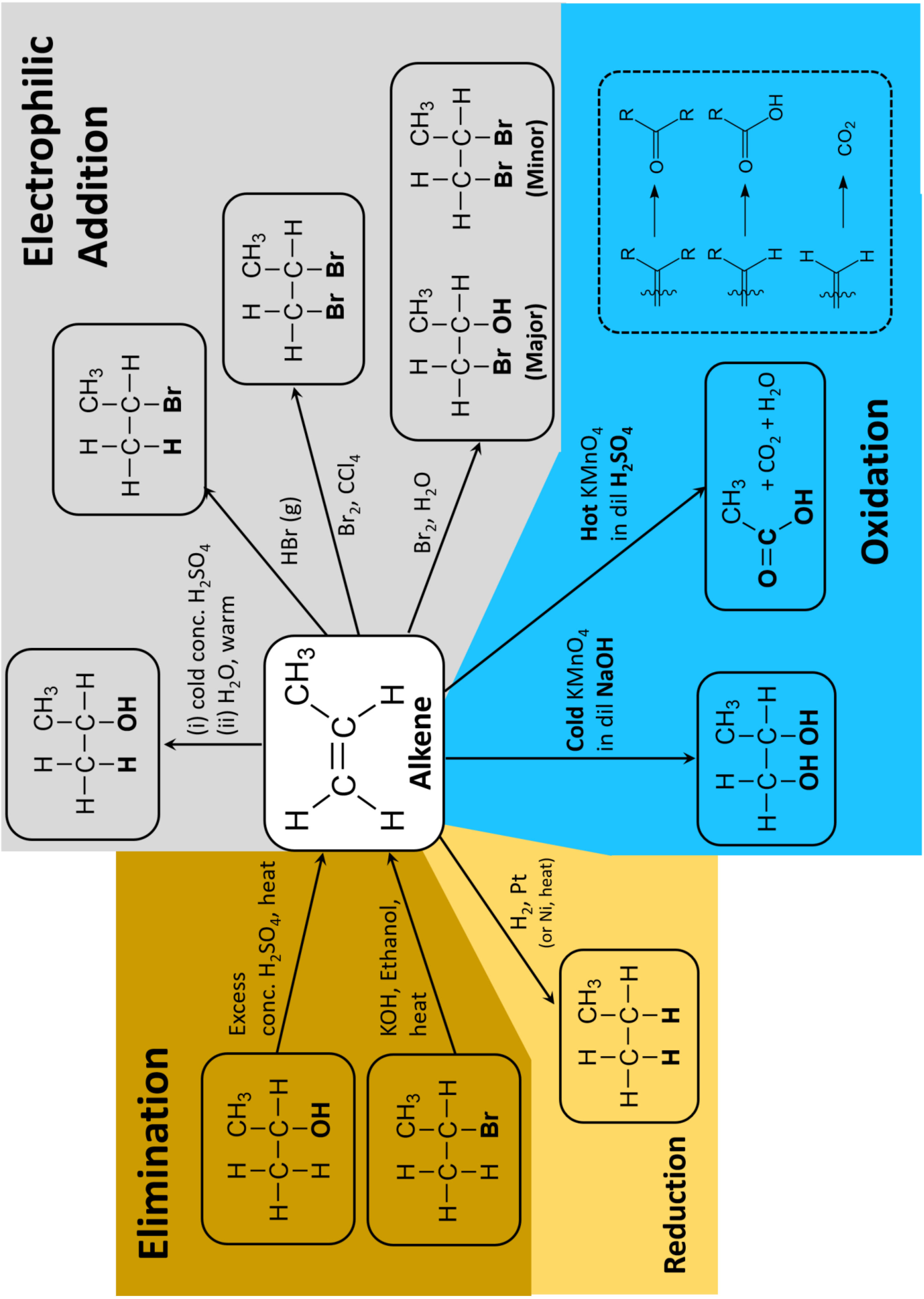
Describe one simple chemical test to distinguish the following set of compounds, stating clearly the **observation** for each compound and support your answer with appropriate **balanced equations**.



and



Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I can deduce the structure of an alkene from its given IUPAC name (and vice versa)	DQ 1,2	
2. I can explain the difference in boiling point and melting point between cis and trans isomers.	DQ13a	
3. I can state the reagents and conditions to convert a. alcohol to alkene b. halogenoalkane to alkene 4. I recognize that elimination of H−X from halogenoalkanes and H−OH from alcohol is only possible between two adjacent carbon atoms. 5. I can give the structure of the alkene formed from the elimination reaction.	KIV	
6. I can state the reagents and conditions for the reactions of alkenes.	DQ11a, 13c	
7. I can deduce the structure of alkenes when the organic products and reagents and conditions are given.	DQ10,12	
8. I can write balanced equations for the reactions of alkenes.	DQ11c	
9. I can explain why alkenes are reactive towards electrophiles. 10. I understand why alkenes tend to undergo addition reactions.	DQ3	
11. I can describe the electrophilic addition mechanism for alkenes using equations, curly arrows and charge when relevant. 12. I can deduce the structure of the major product from electrophilic addition of an alkene in a polar solvent.	DQ5,7	
13. I can describe the use of bromine to test for the presence of C=C functional group.	DQ9	
14. I can predict the major product from electrophilic addition of an asymmetric alkene. 15. I can explain how the major product is formed by considering the stability of carbocation.	DQ4-6	
16. I can understand why the product of electrophilic addition of alkene is optically inactive even if it contains a chiral carbon.	DQ5a,11b	
17. I can give the structure of products formed when alkene reacts with $KMnO_4$ under different conditions.	DQ11c	
18. I can give the observation when an alkene reacts with $KMnO_4$ in alkaline or acidic medium.	DQ9b	
19. I can deduce the structure of the original alkene from the structure of the oxidised fragments of vigorous oxidation reaction.	DQ8, 10c-d	


Electrophilic Addition
Alkene
(i) cold conc. H_2SO_4
(ii) H_2O, warm
HBr (g)
Br_2, CCl_4
Br_2, H_2O
(Major)
(Minor)
Oxidation
Cold $KMnO_4$ in dil NaOH
Hot $KMnO_4$ in dil H_2SO_4
+ CO_2 + H_2O
CO_2
Reduction
H_2, Pt
(or Ni, heat)
Elimination
Excess conc. H_2SO_4, heat
KOH, Ethanol, heat

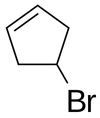
Alkenes Tutorial

Structure and naming

1 Give the IUPAC names of the following compounds.

(a) $(CH_3)_2CHCH{=}C(CH_3)_2$

(b)



2 Draw the structural formulae of the following compounds.

(a) 1-bromo-3-ethylcyclopentene

(b) 3,6-dimethyl-4-propylhepta-1,4-diene

(c) *trans*-hex-2-ene

Electrophilic addition

3 (2021/P1/16) Which statement about propene explains how it reacts with bromine?

A Electrons in the carbon−carbon π bond are donated to an electrophile.

B Electrons in the carbon−carbon σ are donated to an electrophile.

C The sp^2 hybridised carbon is an electrophile and accepts a pair of electrons.

D The σ bond between the sp^2 hybridised carbon atoms is weak and readily broken.

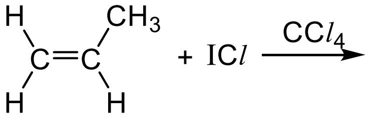
4 For each of the following reactions,

(i) give the structures of the product(s) formed in each of the following reactions.

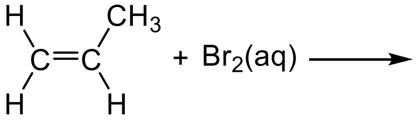
(ii) identify, with explanation, the major product where applicable.

(iii) state the observation during reaction where applicable.

(a)



(b)

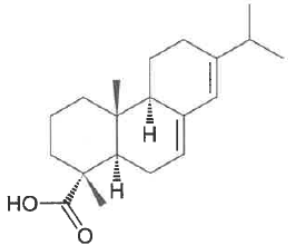


5 Explain each of the following observations, as fully as you can, by making reference to the reaction mechanism of alkenes:

(a) Addition of pure hydrogen iodide to but-1-ene gives a mixture of two enantiomers in equal molar proportions.

(b) Addition of liquid bromine to a solution of ethene in methanol gives a mixture of 1,2-dibromoethane and $CH_2BrCH_2OCH_3$. However, when ethene is shaken with an aqueous solution containing both bromine and sodium chloride, 1,2-dibromoethane, 2-bromoethanol and 1-bromo-2-chloroethane are also formed, but not 1,2-dichloroethane.

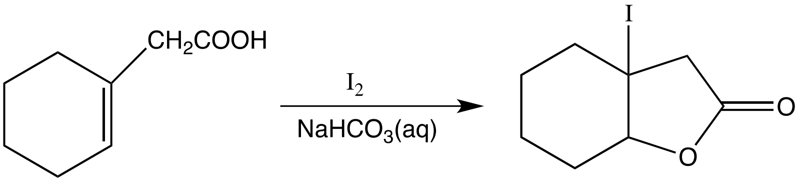
6 (2018 P3 Q4d) Abietic acid is a major component of many resins and has the following structure.



abietic acid, $C_{20}H_{30}O_2$

Draw the structure of the major product when abietic acid is reacted with an excess of HBr. State how many extra chiral centres are formed.

7 When compound **R** is reacted with iodine in the presence of aqueous sodium hydrogencarbonate, iodine does **not** add across the carbon–carbon double bond of compound **R**. Instead, a compound **S**, which has a molecular formula, $C_8H_{11}O_2I$, is formed as shown:



R

S

$NaHCO_3$ function as a *base* during this reaction. Suggest an explanation for the observation.

Oxidation

8 For each of the following, identify the alkene which forms the products upon vigorous oxidation by hot acidified $KMnO_4$, giving its structure and IUPAC name.

Draw the cis-trans isomers of the alkene (if any).

(i) $CH_3CH_2CO_2H$ only

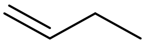
(ii) $(CH_3)_2CO$ and $CH_3CH_2CO_2H$

(iii) CO_2 and $CH_3COCH_2CH_2CH_3$

Distinguishing test

9 Describe one simple chemical test to distinguish each set of compounds, stating clearly the observation for each compound in each chemical test. Support your answers with appropriate balanced equations.

(a) cyclohexane and cyclohexene

(b)  

Application question

10 Suggest, with reasons, a possible structural formula for each of the compounds, **A** – **F**, all of which have the molecular formula C_6H_{12}. Note that no two structures should be the same.

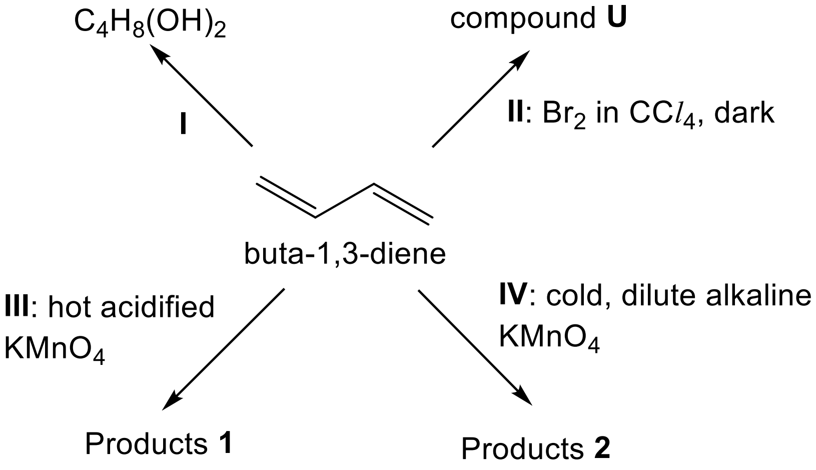
(a) **A** does not decolourises aqueous bromine.

(b) **B** decolourises liquid bromine dissolved in tetrachloromethane and exists as a pair of cis-trans isomers.

(c) **C** undergoes reaction with $KMnO_4$(aq) in dilute acid when heated to give only **one** product, C_3H_6O.

(d) **D** undergoes reaction with $KMnO_4$(aq) in dilute acid when heated to give CH_3CO_2H and $CH_3CH_2COCH_3$.

11 Buta-1,3-diene undergoes the reactions shown in the scheme below



(a) **(i)** Suggest the reagents and conditions for reaction **I**.

(ii) Give the structural formula of the major product formed in reaction **I**.

(b) **(i)** Name the reaction mechansim of reaction **II** and deduce the structure of compound **U**.

(ii) **U** has 2 chiral centers but only 3 stereoisomers. Explain.

(iii) Give 2 reasons why the product mixture from reaction **II** does not exhibit optical activity.

(c) Write balanced equations for reactions **III** and **IV**.

Integrated questions

12 A hydrocarbon, **A**, contains 87.8% carbon and 12.2% hydrogen by mass and has a M_r of 82. **A** decolourises bromine water. In the presence of nickel catalyst, it reacts with hydrogen to form **B**.

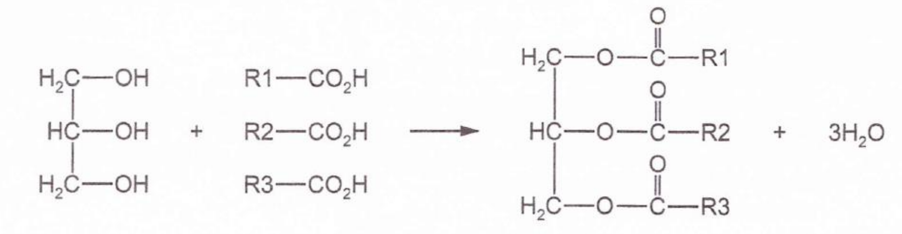
0.1 g of **A** was found to absorb 27.7 cm^3 of hydrogen (measured at s.t.p). **B** does not decolourise bromine water.

(a) Calculate the empirical formula of **A** and hence determine its molecular formula.

(b) Determine the number of moles of hydrogen reacted with 1 mole of **A**. Hence, determine the number of double bonds in a molecule of **A**.

(c) Suggest the structural formulae of **A** and **B**.

13 (Modified from 2016/P2/2) Olive oil contains a mixture of triester formed from glycerol (propane-1,2,3-triol) and three long chain carboxylic acids (fatty acids), as shown by the general equation.



The groups R1, R2 and R3 represent hydrocarbon chains each containing either 15 or 17 carbon atoms. A given oil molecule (triester) can be formed from any combination of the following fatty acids.

name	formula and systematic name	M_r	melting point /°C
palmitic acid	$CH_3(CH_2)_{14}CO_2H$ hexadecanoic acid	256	63
stearic acid	$CH_3(CH_2)_{16}CO_2H$ octadecanoic acid	284	69
oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$ *cis*-9-octadecenoic acid	282	13
linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7CO_2H$ *cis*,*cis*-9,12-octadecadienoic acid	280	–5
linolenic acid	$CH_3CH_2(CH=CHCH_2)_3(CH_2)_6CO_2H$ *cis*,*cis*,*cis*-9,12,15-octadecatrienoic acid	278	–11

(a) A particular triester found in olive oils melts at 15°C.

(i) Explain why this triester melts at a lower temperature than any of the individual fatty acids.

(ii) Trans-9-octadecenoic acid melts at 44°C. Explain the difference in its melting point with cis-9-octadecenoic acid.

(iii) State how the presence of C=C bonds affects the melting point of the fatty acids.

(b) The average number of C=C bonds per molecule in different oils can be compared experimentally by determining the mass of iodine that reacts with 100g of the oil.
In one experiment, 0.256g of olive oil was found to react with 0.237g of iodine.

(i) State the name of the mechanism for the reaction occurring between iodine and the C=C bonds in the olive oil.

(ii) Calculate the mass of iodine that would react with the 100g of olive oil.

(iii) Use your answer from b(ii) to calculate the average number of C=C bonds in each oil molecule in olive oil. The average Mr of an olive oil molecule is 782. Give your answer to three significant figures.

(iv) The triesters in olive oil are formed mainly from oleic acid.

Use this information and the data in the table on page 22 to explain the significance of your answer to b(iii) with respect to the composition of olive oil.

(c) Olive oil can be used to make margarine. Part of the manufacturing process involves decreasing the number of C=C bonds in the oil.

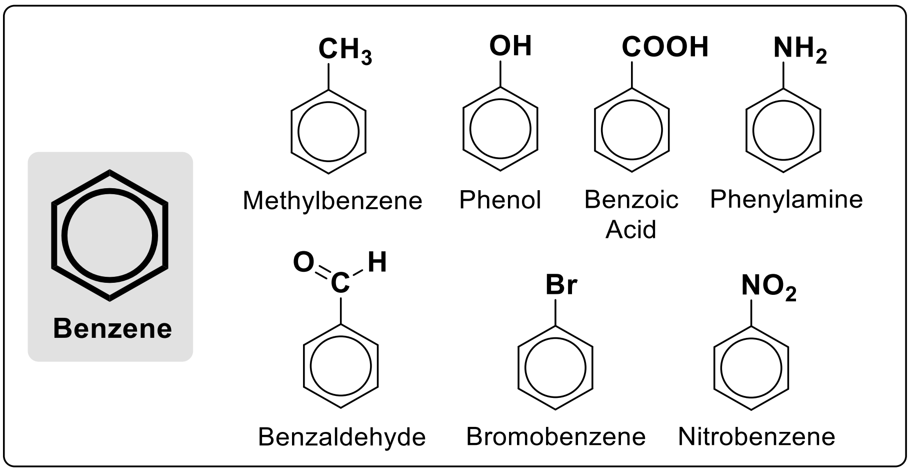
(i) State suitable reagents and conditions to carry out this process.

(ii) The conditions in c(i) can also result in isomerization of the C=C bonds, to form trans fatty acids.
Draw a skeletal formula to show the trans isomer of oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$.

5 ARENES

5.1 INTRODUCTION

- Arenes are a family of aromatic hydrocarbon compounds containing benzene rings with delocalised π electrons.
- Benzene is a member of the arene family with the molecular formula of C_6H_6.



5.2 PHYSICAL PROPERTIES OF BENZENE (C_6H_6)

- Colourless, highly flammable liquid
- Has a characteristic pleasant smell.
- Boiling point: 80.1 °C.
- Non-polar in nature. Hence, soluble in non-polar organic solvents and insoluble in polar solvents.
- Highly toxic and carcinogenic. Long-term inhalation of its vapour can cause anaemia and leukaemia.

Benzene was first isolated as oily residue derived from the production of illuminating gas, and identified by English Chemist, Michael Faraday in 1825, and was first named as ‘bi-carburet of hydrogen’

For interests:
Use of 4n+2 rule to determine aromatic compound

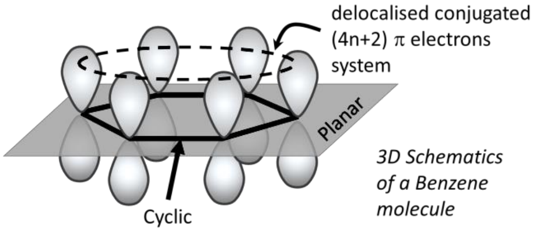
Why are arenes known as aromatic compounds?

The term ‘aromatic compound’ was first used by August Wilhelm von Hofmann (*left picture*) in his description of phenyl radical in 1855. It is unknown why he had chosen this term but many of the earliest known examples of arenes did have distinctively pleasant fragrance.

However, the term ‘aromatic’ is used today to describe **planar**, **cyclic molecules** with **enhanced stability due to delocalised conjugated (4n+2) π electrons system** and have no relation with smell.

Note:
Each C atom of benzene is bonded to 1 H atom.

2D view of Benzene molecule



3D Schematics of a Benzene molecule

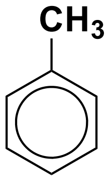
5.3 Nomenclature of Arenes (Self-read)

Success criteria:
• I can deduce the structure of an arene from its given IUPAC name (and vice versa).

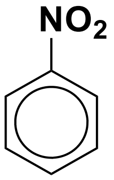
There are multiple naming systems for arenes. IUPAC naming system is most frequently and widely used for reference to the different aromatic compounds. However, for certain benzene derivatives, common names are used instead for convenience or simply a matter of tradition.

A. Monosubstituted Benzenes

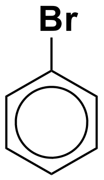
- For many simple monosubstituted benzene, the **benzene ring is considered as the parent chain**. In such cases, 'benzene' is placed as suffix, while the substituents as prefix.



Methylbenzene

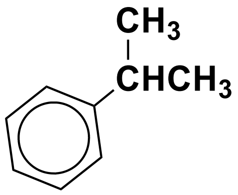


Nitrobenzene

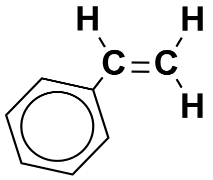


Bromobenzene

- When the substituent is too complex to be named as the prefix, the benzene ring will be treated as the substituent instead and is named as 'phenyl'.

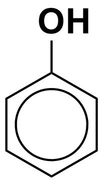


2-**phenyl**propane

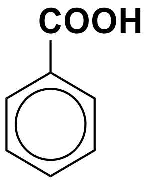


Phenylethene

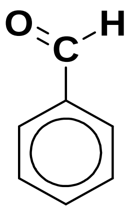
- Some of the monosubstituted benzenes are known by their **common names**. (Will be covered in subsequent chapters)



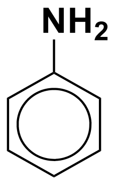
Phenol



Benzoic acid



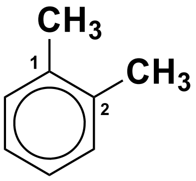
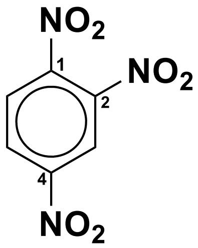
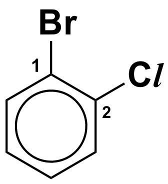
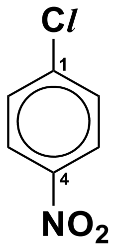
Benzaldehyde



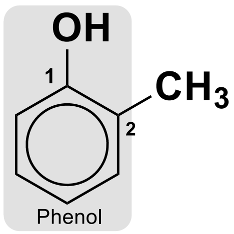
Phenylamine

B. Polysubstituted Benzenes

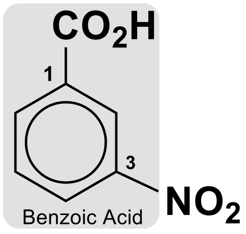
- The position number of substituents assigned should be as small as possible if there is more than one substituent.

Identical substituents	**Different substituents**
• Indicate using number, the positions of all substituents • Indicate no. of substituents using di, tri, etc.	• Substituents are arranged in alphabetical order according to the first letter of the prefix of the substituents • Indicate using number, the positions of all substituents with the first prefix taking the smallest no.
 1,2-**di**methylbenzene  1,2,4-**tri**nitrobenzene	 1-**b**romo-2-**c**hlorobenzene  1-**c**hloro-4-**n**itrobenzene

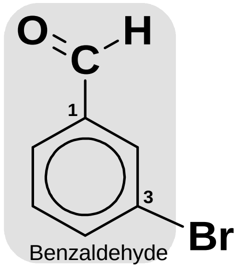
- For polysubstituted benzene derivatives with common names, the 'other substituents' are stated as prefixes and arranged in the direction which gives the lowest possible numbers relative to the carbon with the highest priority functional group.



2-methyl**phenol**



3-nitro**benzoic acid**



3-bromo**benzaldehyde**

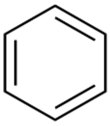
5.4 STRUCTURE OF BENZENE

Success criteria:
• I understand that benzene exist as a resonance structure from its experimental (i) bond length and (ii) enthalpy change of hydrogenation. • I can explain the resonance stability of benzene that results from the continuous side-way overlap of the unhybridised p-orbital of the 6 sp^2 hybridised carbon atoms in benzene.

The structure of Benzene posed a huge problem for 19th century chemists. Many theories were put forth but the structure of benzene was confirmed only in 1925 (a century after the discovery of benzene) through X-ray crystallography.

5.4.1 Kekule's structure

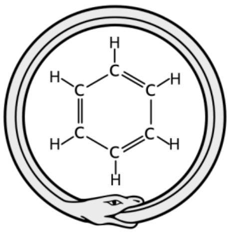
- **Friedrich August Kekulé** in 1865 proposed **cyclohexa-1,3,5-triene** as the structure of benzene. Kekule's structure is also the earliest and the most accurate proposed structure of benzene amongst the work of the other chemist of his time.



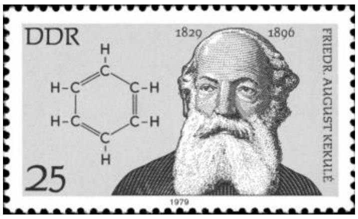
cyclohexa-1,3,5-triene

Despite being the closest to the actual structure of benzene, Kekule's structure is still incorrect. Two experimental evidences (bond length and enthalpy change of hydrogenation of benzene) suggest Kekule's structure is still flawed.

How did Kekulé came up with the structure? (FYI)



In an event organised by German Chemical Society in 1890 celebrating the 25th anniversary of Kekulé's first benzene paper, Kekulé shared that he discovered the ring structure of benzene after nodding off as he was trying to resolve the structure and had a day-dream. In his day-dreams, he saw a snake coiled up, grabbing its own tail (a symbol known in many ancient cultures as Ouroboros). This struck him that benzene might be a 'ring'.

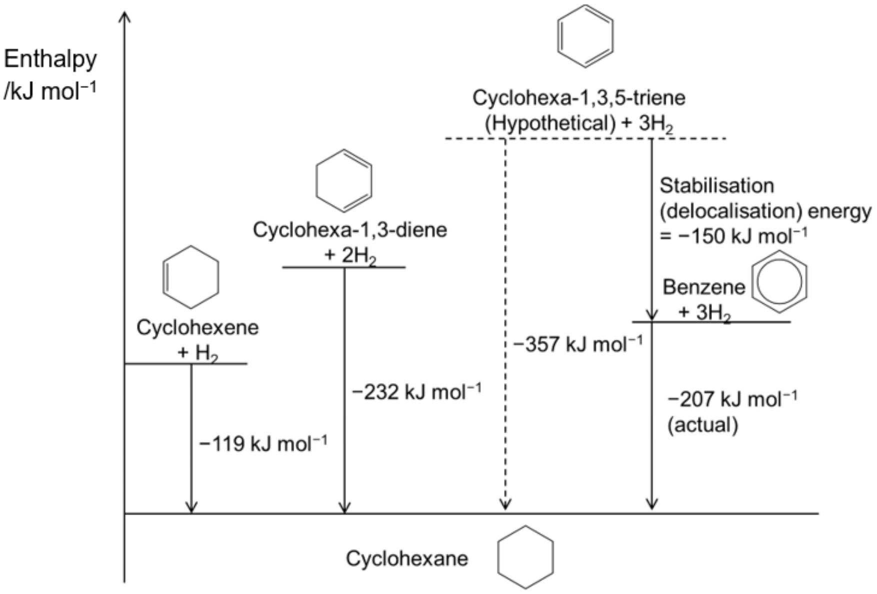


Kekulé supported his proposed structure with the observation that monosubstituted benzene always appeared as one isomer and there are exactly three isomers of every disubstituted derivative (now known to be substituents in the ortho(2), meta(3) and para(4) position). His ring structure was also able to explain benzene's 1:1 C-H ratio.

(i) Enthalpy change of hydrogenation of benzene *(FYI)*

Predicted enthalpy change of hydrogenation of benzene	
Enthalpy change of hydrogenation of **cyclohexene** $C_6H_{10} + H_2 \rightarrow C_6H_{12}$	– 119 kJ mol^{-1}
Enthalpy change of hydrogenation of cyclohexa-1,3-diene $C_6H_8 + 2H_2 \rightarrow C_6H_{12}$	– 232 kJ mol^{-1} (~2 times the value of enthalpy change of hydrogenation of cyclohexene)
If Kekule's structure is correct,	
Enthalpy change of hydrogenation of cyclohexa-1,3,5-triene $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$	**– 357 kJ mol^{-1}** (~3 times the value of enthalpy change of hydrogenation of cyclohexene)

Experimental Data
However, the enthalpy of hydrogenation of benzene was determined to be **– 207 kJ mol^{-1}**.
What could have contributed to the additional stability of benzene? Resonance gives additional stability to benzene, this leads to a smaller difference in the energy level of benzene and cyclohexane. Thus, a lower-than-expected magnitude of enthalpy of hydrogenation is obtained experimentally. Resonance refers to the delocalization of π electrons. A stronger attraction is formed between the nuclei and the delocalised π electrons, giving rise to additional stability.



Energy Level Diagram showing the added stability due to resonance

(ii) Bond Length

Ponder…
What is the bond order of the C-C bonds in benzene?

Predicted Properties	Experimental Data
Based on Kekule’s structure, we would expect benzene to possess 3 single C–C and 3 double C=C bonds. As such, we would expect benzene to have alternating shorter C=C double bonds (134 pm) and longer C–C single bonds (147 pm).	Experimental evidence showed that all the 6 carbon-carbon bonds in benzene are of equal length (139 pm) which are intermediate in length between single C-C and C=C double bonds. This is contrary to what is expected!!

5.4.2 Resonance structure of Benzene

How do you tell that carbon is sp^2 hybridised in benzene?

- All the carbon atoms in benzene are **sp^2 hybridised**, and the entire molecule is planar in shape.

- The unhybridised p orbital of each C atom contains 1 electron and lie perpendicular to the plane of the benzene ring (see Figure 1).

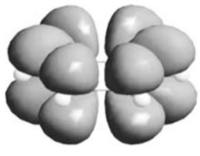


Figure 1

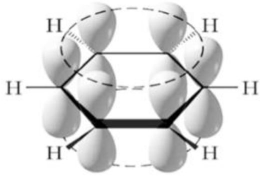


Figure 2

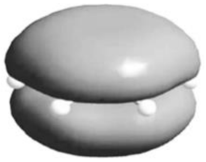
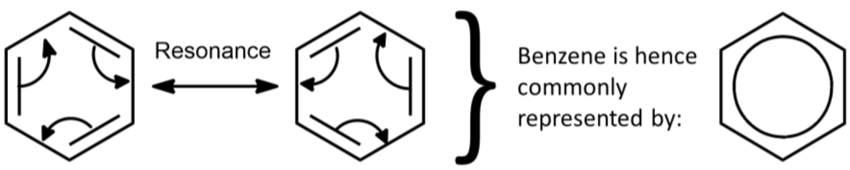


Figure 3

- Continuous side-way overlap of the unhybridised p-orbital results in two doughnut-shaped electron clouds lying above and below the ring. (see Figure 2 and 3)

- This causes the 6 π electrons in benzene to be delocalised throughout the entire ring structure, giving rise to **aromatic stability**.

- Benzene is thus a resonance hybrid of two equivalent Kekule’s structures (see Figure 4) This resonance structure brings about enhanced chemical stability.



Benzene is hence commonly represented by:

Figure 4

5.5 CHEMICAL PROPERTIES OF BENZENE

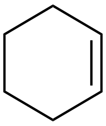
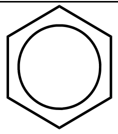
5.5.1 Differences in reactivity of Alkene and Benzene

Success criteria:
• Using the concept of delocalisation of π-electron, I can explain why benzene (i) undergoes substitution instead of addition reaction and (ii) exhibits lower reactivity towards electrophile compared to alkene.

Due to the presence of delocalised π electron cloud, benzene reacts differently from the other unsaturated organic compounds.

Structure	Implication on Reactivity
Benzene consists of **delocalised π electrons** above and below the plane.	Less susceptible to attack by **electrophiles** ⇨ Requires a **stronger electrophile** (eg. Br^+ instead of polarised Br_2) to react.
The ring of delocalised π electrons gives benzene additional **aromatic stability**.	Addition Reaction that destroys the aromatic ring **requires an additional input of energy** and is thus unfavourable. ⇨ Undergoes **substitution reaction** to preserve aromatic stability.

Table 1: Difference in reactivity between alkene and benzene

Reagents	 **Cyclohexene**	 **Benzene**
Br_2 (*l*) in CCl_4	Decolourisation of orange-red Br_2 (*l*)	Orange-red Br_2 (*l*) remains.
Cold $KMnO_4$, NaOH(aq)	Decolourisation of purple $KMnO_4$; Brown ppt of MnO_2 observed	Purple $KMnO_4$ remains.
Hot $KMnO_4$, H_2SO_4(aq)	Decolourisation of purple $KMnO_4$	Purple $KMnO_4$ remains.

5.5.2 Combustion

In sufficient oxygen, benzene burns completely to give carbon dioxide and water.

$$C_6H_6\ (l) + \frac{15}{2}O_2\ (g) \rightarrow 6CO_2\ (g) + 3H_2O\ (l)$$

Due to high C:H ratio (≈1:1), benzene-containing compounds burn with a sooty flame because of insufficient oxygen for complete combustion.

$$C_6H_6\ (l) + \frac{3}{2}O_2\ (g) \rightarrow \mathbf{6C\ (s)} + 3H_2O\ (l)$$

Benzene content in petrol to be cut, *Straits Times*, Jan 14, 2016

Environmental and Health Impact of Benzene (FYI)

Benzene is used in petrol additive as a substitute for tetraethyl lead in leaded petrol to reduce harm to the environment. It increases the octane rating and reduces knocking. It was initially thought of as a good substitute which results in lesser health hazard. However, with the finding of benzene as a carcinogen, the negative health effects and possibility of benzene entering ground water, stringent regulation of benzene content in petrol have been imposed.

In Singapore, NEA imposed a new specification that benzene in petrol should not exceed 1 per cent in volume from early 2016.

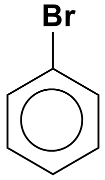
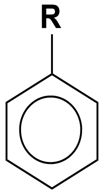
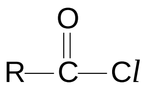
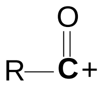
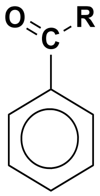
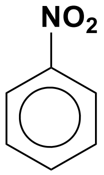
5.5.3 ELECTROPHILIC SUBSTITUTION REACTIONS**

Success Criteria:

- I can state the reagents and condition required for the electrophilic substitution of a C-H bond in benzene with halogen atom, alkyl group, acyl group and nitro group respectively.
- I am able to deduce the structure of the electrophile and hence, the substituted product formed from a given set of reagents and condition.

- Benzene typically undergoes catalyzed **electrophilic substitution** reactions.

Table 2: Overview of various electrophilic substitution reactions

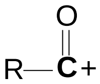
Reaction/ reagents	Electrophile used in the substitution	Product
Halogenation e.g. Br_2 with anhydrous $FeBr_3$ catalyst	$\mathbf{Br^+}$	
Alkylation e.g. RCl with anhydrous $FeCl_3$ catalyst	$\mathbf{R^+}$	
Acylation e.g.  $R-\overset{\overset{\displaystyle O}{\Vert}}{C}-Cl$ with anhydrous $FeCl_3$ catalyst	 $R-\overset{\overset{\displaystyle O}{\Vert}}{\mathbf{C}}+$	
Nitration Conc. HNO_3 with conc H_2SO_4 catalyst, 55−60°C	$^{+}\mathbf{N}O_2$	

Success criteria:
• I can describe the mechanism of electrophilic substitution with the use of equations, showing the following clearly: (i) Generation of strong electrophile (ii) Curly arrow to show the formation of arenium carbocation in the slow step. (iii)Curly arrow to show regain of aromaticity and regeneration of catalyst.

(i) General Mechanism of Electrophilic Substitution

Step 1: Generation of strong electrophile (E^+)

Note:
Al in $AlCl_3$ is electron-deficient (short of octet in the valence shell), hence it behaves as a *Lewis Acid, accepting an electron pair.*
(Lewis acid definition will be covered in Acid-base Equilibrium chapter)

(a) **X^+, R^+ or**  **(Halogen or alkyl or acyl cation)**

$R-\overset{\overset{\displaystyle O}{\|}}{C}{}^+$

Generated by **Lewis acid catalyst** (i.e. $AlCl_3$, $FeBr_3$).

$$AlCl_3 + Cl_2 \longrightarrow Cl^+ + AlCl_4^-$$

$$FeBr_3 + CH_3CH_2Br \longrightarrow CH_3\overset{+}{C}H_2 + FeBr_4^-$$

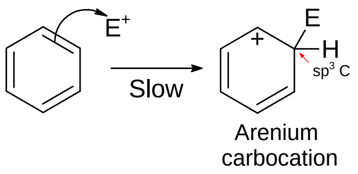
(b) **$^+NO_2$**

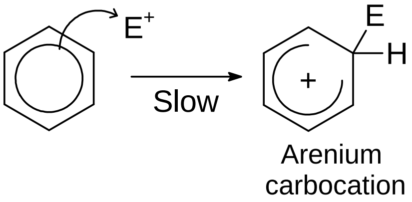
Generated through the use of **conc. HNO_3 and conc. H_2SO_4**

$$HNO_3 + H_2SO_4 \longrightarrow H_2O + {}^+NO_2 + HSO_4^-$$

Step 2: Electrophilic attack of E^+ on benzene, forming the reactive arenium carbocation intermediate. (SLOW STEP)

For visualization:



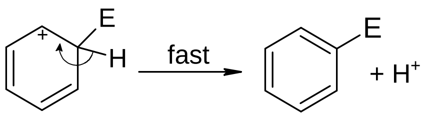


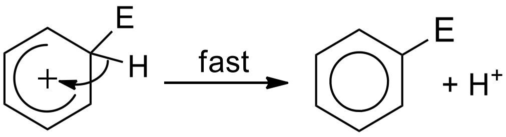
- Two of the six π electrons are used to form a dative bond with E^+. This leaves four π electrons delocalized over the remaining five carbon atoms in the positively charged arenium carbocation intermediate.

- The carbon atom that forms a bond with the incoming E^+ becomes sp^3 hybridised. It no longer has the unhybridised p-orbital to form a continuous overlap with the p orbitals of other carbon atoms. Aromatic stability is disrupted.

Step 3: Loss of H^+ to regain aromaticity and regeneration of catalyst. (FAST STEP)

For visualization:





- All the carbon atoms become sp^2 hybridised again and the benzene ring is restored to achieve aromatic stability.

- Catalyst is regenerated (not shown here).

Checkpoint 1

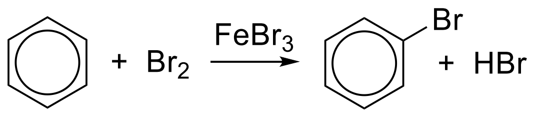
The pi electrons in both alkenes and benzene causes them to react with electrophiles. Why can't benzene react with weak electrophiles such as Br_2 directly but require a catalyst to generate Br^+?

Answer:

For benzene, the π electrons are ____________________for reaction compared to the π electrons of alkene due to __________________ in benzene. Thus, the halogen carrier catalyst is required so as to generate Br^+ (full positive charge), which is _________________ electrophilic than a polarized Br_2 (partial charge).

(ii) Specific Examples of Electrophilic Substitution

- **HALOGENATION**



Type of reaction	Electrophilic Substitution
Reagent and condition	Br_2 with anhydrous $FeBr_3$ catalyst OR Cl_2 with anhydrous $FeCl_3$ (or $AlCl_3$) catalyst

Note:
Anhydrous condition is needed such that $AlCl_3$ can act as a Lewis acid and react with Cl_2 to generate strong electrophile Cl^+.
If H_2O is present, $AlCl_3$ would react with H_2O to give $[Al(H_2O)_6]^{3+}$ and loses the ability to react with Cl_2.

Important

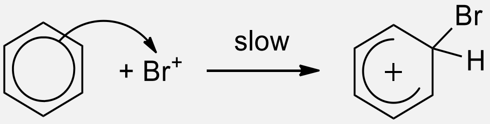
(i) State the name of mechanism
(ii) Show reaction with catalyst to generate strong electrophile
(iii) Arrows ALWAYS flow from ***electron rich region (π electron cloud of benzene or lone pair of nucleophiles***) to electron deficient region (electrophile)
(iv) Indicate the slow step
(v) Show regeneration of catalyst

Mechanism: ELECTROPHILIC SUBSTITUTION

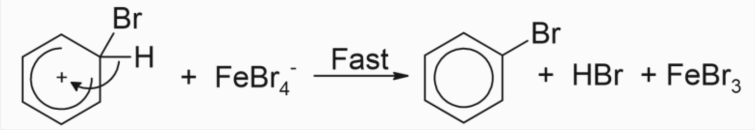
Step 1: Generation of strong electrophile (Br^+)

$$\mathbf{Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^-}$$

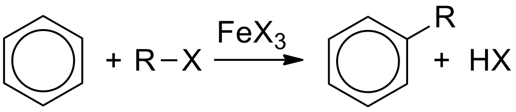
Step 2: Electrophilic attack of Br^+ on benzene, forming the arenium carbocation intermediate. (SLOW step)



Step 3: Loss of H^+ to regain aromaticity and regeneration of catalyst.



- **Friedel-Crafts ALKYLATION (formation of alkylbenzene)**



Type of reaction	Electrophilic Substitution
Reagent and condition	RX with anhydrous FeX_3 (or AlX_3) catalyst

Check your mechanism:

(i) State the name of mechanism
(ii) Show reaction with catalyst to generate strong electrophile
(iii) Arrows ALWAYS flow from ***electron rich region (π electron cloud of benzene or lone pair of nucleophiles***) to electron deficient region (electrophile)
(iv) Indicate the slow step
(v) Show regeneration of catalyst

Checkpoint 2

Describe the mechanism for the formation of methylbenzene from benzene using CH_3Br and $FeBr_3$ catalyst.

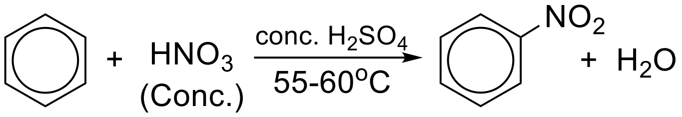
Name of Mechanism:

Step 1: Generation of strong electrophile ($^+CH_3$)

Step 2: Electrophilic attack of $^+CH_3$ on benzene, forming the arenium carbocation intermediate. (SLOW step)

Step 3: Loss of H^+ to regain aromaticity and regeneration of catalyst.

- **NITRATION (Formation of nitrobenzene)**



Type of reaction	Electrophilic Substitution
Reagent and condition	Conc HNO_3 , conc H_2SO_4, 55−60°C

Note :
Conc H_2SO_4 only lose one H^+ in Step 1.

Important
(i) State the name of mechanism
(ii) Show reaction with catalyst to generate strong electrophile
(iii) Arrows ALWAYS flow from ***electron rich region (π electron cloud of benzene or lone pair of nucleophiles***) to electron deficient region (electrophile)
(iv) Indicate the slow step
(v) Show regeneration of catalyst

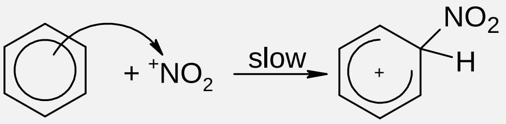
As conc. H_2SO_4 is a stronger acid than HNO_3, it serves as the acid, while HNO_3 behaves as a base.

Mechanism: Electrophilic substitution

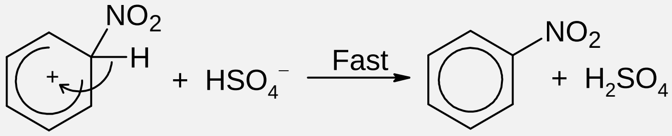
Step 1: Generation of strong electrophile ($^+NO_2$).

$$HNO_3 + H_2SO_4 \longrightarrow H_2O + {}^+NO_2 + HSO_4^-$$

Step 2: Electrophilic attack of $^+NO_2$ on benzene, forming the arenium carbocation intermediate. (SLOW step)



Step 3: Loss of H^+ to regain aromaticity and regeneration of catalyst.



Practical Consideration (For your info)

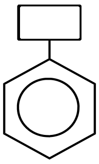
Since nitro group is deactivating in nature, it is easy to stop the reaction at monosubstitution. However, a second or third nitro group can be introduced, especially when an activating substituent is present on the benzene ring.

Nitrations are usually carried out at comparatively low temperatures as the oxidizing action of nitric acid may result in lower yield if the reaction is carried out at higher temperature.

The aromatic substrate is usually added slowly portion-wise to the nitrating mixture. This is because the heat generated from the reaction may result in undesirable poly-nitration, should monosubstituted product be desired. The mixture may even be cooled in an ice water if necessary. Only after all the substrates had been added will the mixture be allowed to warm to the stipulated temperature.

Example:
In the case of benzene and naphthalene, reaction is maintained at ~50 °C during addition of the aromatic hydrocarbon and only thereafter, heated in water bath at ~60 °C for 45 minutes to complete the reaction.

5.6 BENZENE DERIVATIVES



A substituent/group already present on the benzene ring has two effects:

A. It affects the reactivity of the benzene ring.

B. It affects the orientation of electrophilic substitution by directing the next incoming electrophile to a specific position on the benzene ring.

5.6.1 Effects of Substituent on Rate of Electrophilic substitution

Success criteria:
• I can explain the reactivity of benzene towards electrophile by considering the electronic effect of the substituents on the electron density of the benzene ring. • I am able to (i) predict the conditions required (ii) devise a correct sequence of steps to form a poly-substituted product of electrophilic substitution by considering the electronic and directing effect of the substituent in mono-substituted benzene.

Activating groups substituents that *donate* electron density to the benzene ring	**Deactivating groups** substituents that *withdraw* electron density from the benzene ring
• Increase the electron density of the ring and activate the ring • Make the ring more susceptible (more reactive) to electrophilic attack	• Decrease the electron density of the ring and deactivate the ring • Make the ring less susceptible (less reactive) to electrophilic attack
➢ **Increase the rate** of electrophilic substitution ➢ Requires a **milder condition** for reaction.	➢ **Decrease the rate** of electrophilic substitution ➢ Requires a **harsher condition** for reaction.

5.6.2 Effects of Substituent on Orientation of Electrophilic Attack

- Depending on the group already on the benzene ring, the attack can either be mainly directed at the **2,4-positions** or the **3-position.**

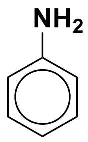
Note:
A summary of this can also be found inside the *Data Booklet*

2,4-directing			**3-directing**
Strongly Activating	**Weakly Activating**	**Weakly Deactivating**	**Deactivating**
Groups containing N and O atoms with lone pairs which can be delocalised into the benzene ring	Groups that are electron-donating inductively	Groups that are highly electronegative and electron-withdrawing inductively	Groups containing multiple bonds to electronegative atoms
e.g. $–NH_2$, $–NHR$, $–OH$ or $–OR$	Alkyl groups e.g. $–CH_3$	Halogen groups e.g. $–Cl$, $–Br$	e.g. $–NO_2$, $–CHO$, $–COR$, $–CO_2H$, $–CN$

Table 3: Summary of effects of substituents on electrophilic attack

Checkpoint 3

1 Rank the following aromatic compounds in term of increasing reactivity towards electrophilic substitution. (1 being the most reactive and 3 being the least reactive)



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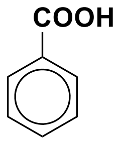

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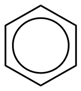

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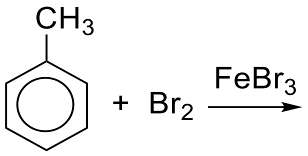
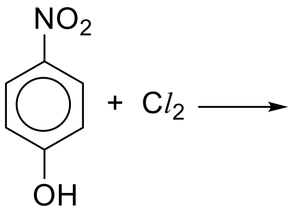
2 Draw the structures of the major products formed from the reactions below.

(a)



(b)



Note:
Strongly activating group (like −OH, $-NH_2$) allows electrophilic substitution reaction to occur without presence of catalyst (More info in Chapter 7 (phenol) and Chapter 10 (phenylamine)

3 Propose a synthetic route to synthesize 3-bromonitrobenzene from benzene, stating the reagents and conditions for each step.

How is a substituent either electron donating or electron withdrawing?(FYI)

Electron density can either be donated or withdrawn through the following 2 effects:

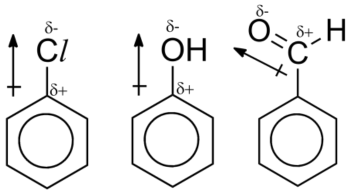
(i) Inductive effect
(ii) Resonance effect

(i) Inductive effect

occurs when there is *electronegativity difference* between the bonding atoms.

Inductive effect can be understood as the **withdrawal** or **donation of electrons through a σ bond** due to **electronegativity** and the polarity of bonds in functional groups.

In a bond between carbon and an element **X**, if **X** is more electronegative than carbon, **X** is said to have a negative inductive effect.



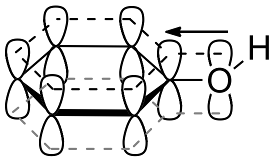
For instance, halogens, carbonyl groups and cyano groups contain electronegative atoms and **inductively withdraw** electrons through the σ bond (as shown on right).

Alkyl groups are electron-donating, and are said to have a positive inductive effect.

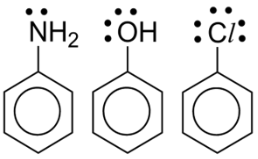
(ii) Resonance effect:

occur with *at least a lone pair of electrons* in the p-orbital of the substituent.

Resonance effect is the withdrawal or donation of electrons **through a π bond** due to overlap of a p orbital on the substituent with a p orbital on the adjacent double bond or benzene ring.



Donating of electron density from O into the benzene ring.



Substituents which donate electrons by resonance include amino, hydroxyl and halogen groups.

<u>Overall electronic effect on benzene.</u>

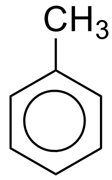
Whether a substituent is electron-donating or electron-withdrawing *depends on the* ***overall*** *inductive and resonance effect.* For groups which are electron withdrawing inductively but electron donating by resonance (or vice versa), the factor which dominates will ‘win’.

For example,

1) $-NH_2$ and $-OH$ groups has **overall electron donating** effect on benzene.
N and O are in Period 2. . A more effective lateral overlap of the 2p orbitals between C and N or between C and O causes resonance effect (e^- donating) to **outweigh** inductive effect (e^- withdrawing).

2) halogens has **overall electron-withdrawing** effect on benzene.
Halogens (ie, C*l*, Br, I) are in Period 3 and below. A less effective lateral overlap between the larger 3p/4p/5p orbital of X atom and 2p orbital of the sp^2 hybridised carbon, as compared to the 2p-2p overlap in C−O, results in weak resonance effect. Thus, inductive effect (e^- withdrawing) outweighs the weak resonance effect (e^- donating).

5.6.3 Important Benzene Derivative: Methylbenzene



Methylbenzene

Reactions involving Methylbenzene

Reactions of methylbenzene can be on the
(i) on the benzene ring and,
(ii) methyl group (also known as the alkyl side chain).

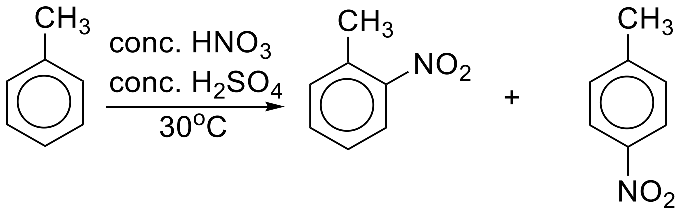
In the following section, we will learn the types of reactions possible on both positions.

(i) Reactions Involving the ***Benzene Ring* of methylbenzene**

- Benzene ring will undergo **Electrophilic Substitution** with mechanism as per described in the previous section.
- However, since the methyl group is weakly electron-donating, it increases the electron density of the benzene ring. As such, methylbenzene is slightly more reactive than benzene towards electrophilic attack.
- **Milder conditions are required for nitration.**
- Methyl substituent is **2,4-directing.** Hence, **2 products will be formed** from the electrophilic substitution.

(a) Nitration of methylbenzene

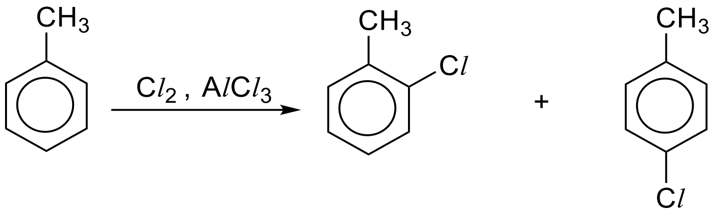
Note: As alkyl group are weakly electron donating group, catalyst is still required to generate the strong electrophile. Only difference is that nitration of alkylbenzene can occur at a lower temperature.



1-methyl-2-nitrobenzene 1-methyl-4-nitrobenzene

Type of reaction	Electrophilic Substitution
Reagent and condition	Conc HNO_3, conc H_2SO_4 , 30°C

(b) Halogenation of methylbenzene



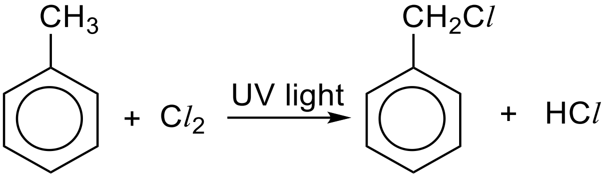
1-chloro-2-methylbenzene 1-chloro-4-methylbenzene

Type of reaction	Electrophilic Substitution
Reagent and condition	Br_2 with anhydrous $FeBr_3$ catalyst OR Cl_2 with anhydrous $FeCl_3$ (or $AlCl_3$) catalyst

(ii) Reactions Involving the Alkyl Side Chain of Alkylbenzene

(a) Free Radical Substitution

What product would be obtained with excess Cl_2?



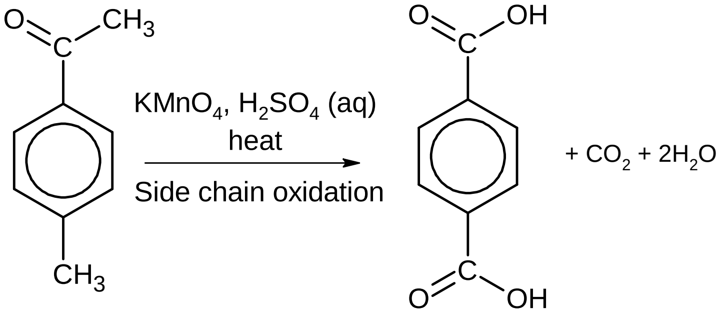
Type of reaction	Free Radical Substitution
Reagent and condition	Cl_2 (g), UV light / heat

(b) Oxidation of Alkyl Side-chain of alkylbenzene

Success criteria:
For alkyl side chain oxidation, I am able to provide the following: • structural requirement of alkyl side chain • reagents and conditions • structure of the oxidised product in the acidic or alkaline medium. • observations that come with the products formed. • balanced equation using [O] and H_2O.

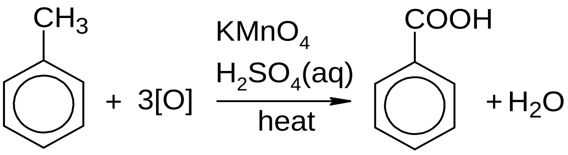
- While alkane is resistant to oxidation by $KMnO_4$, the alkyl side chain of a benzene maybe oxidized by $KMnO_4$ depending on the structure of the alkyl side chain.

- As long as the **C atom directly attached to the benzene ring has at least a H or O**, the alkyl side chain will be oxidised to a carboxyl group, –COOH.



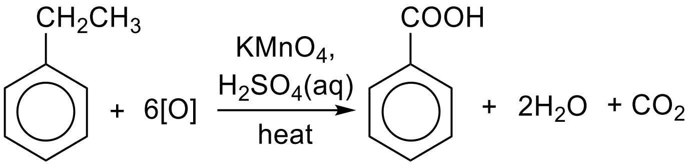
In acidic medium

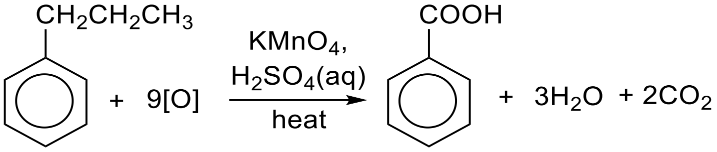
Note:
[O] is used on the reactant side to balance the oxidation equation



Type of reaction	Oxidation
Reagent and condition	$KMnO_4$, H_2SO_4(aq), heat
Observation	Decolourisation of purple $KMnO_4$

Is it possible to distinguish methylbenzene with other alkyl benzene?

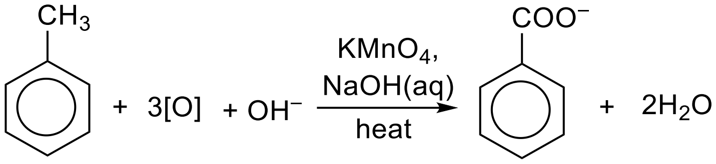




***Vigorous oxidation of any alkylbenzene results in formation of benzoic acid.*

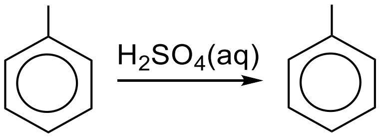
In alkaline medium

Note:
In alkaline medium, the conjugate base of benzoic acid, benzoate ion, is formed instead. Reduction of $KMnO_4$ in alkaline medium would produce brown ppt MnO_2.



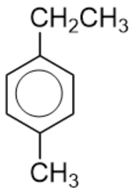
Type of reaction	Oxidation
Reagent and condition	$KMnO_4$, NaOH(aq), heat
Observation	Decolourisation of purple $KMnO_4$, formation of brown ppt MnO_2

- Acidification of the carboxylate salt (e.g. with H_2SO_4) is needed to obtain benzoic acid.

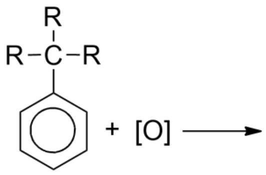


Checkpoint 4

(a) Write a balanced equation for the oxidation of the following alkylbenzene using $KMnO_4$ in acidic medium.



(b) State what would you observe when you subject the following molecule to $KMnO_4$ oxidation in acidic medium. Explain your answer.



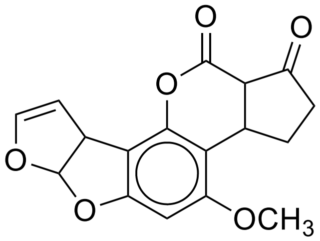
Success Criteria	Relevant Tutorial questions	What do you still struggle with? Write your queries here.
1. I can deduce the structure of an arene from its given IUPAC name (and vice versa).	-	
2. I understand that benzene exist as a resonance structure from its experimental (i) bond length and (ii) enthalpy change of hydrogenation. 3. I can explain the resonance stability of benzene that results from the continuous side-way overlap of the unhybridised p-orbital of the 6 sp^2 hybridised carbon atoms in benzene.	-	
4. Using the concept of delocalisation of π-electron, I can explain why benzene (i) undergoes substitution instead of addition reaction and (ii) exhibits lower reactivity towards electrophile compared to alkene.	DQ1, 2	
5. I can describe the mechanism of electrophilic substitution with the use of equations, showing the following clearly: (i) Generation of strong electrophile (ii) Curly arrow to show the formation of arenium carbocation in the slow step. (iii) Curly arrow to show regain of aromaticity and regeneration of catalyst.	DQ3,5,8	
6. I can explain the reactivity of benzene towards electrophile by considering the electronic effect of the substituents on the electron density of the benzene ring.	DQ4,5a	
7. I am able to (i) predict the conditions required (ii) devise a correct sequence of steps to form a poly-substituted product of electrophilic substitution by considering the electronic and directing effect of the substituent in mono-substituted benzene.	DQ5a,7	
8. For alkyl side chain oxidation, I am able to provide the following: • structural requirement of alkyl side chain • reagents and conditions • structure of the oxidised product in the acidic or alkaline medium. • observations that come with the products formed. • balanced equation using [O] and H_2O.	DQ6	
9. I can predict the structure of the major product of electrophilic substitution based on stability of the intermediate arenium carbocation	DQ3,8,9	

Aromatic Compounds in Real Life Context

1 Aflatoxin & Liver Cancer

(extracted from http://www.niehs.nih.gov/about/congress/impacts/aflatoxin/index.cfm)

For almost four decades, NIEHS-scientists have conducted extensive research on liver cancer of aflatoxin, a naturally occurring toxin. Their discovery of the genetic changes that result from aflatoxin exposure have led to a better understanding of the link between aflatoxin and cancer risk in humans. These discoveries are also being used in developing cancer prevention strategies.



Aflatoxin B_1

Aflatoxin is produced by a mold, *Aspergillus flavus*, which grows on crops such as corn, dried chilli peppers, and peanuts. Aflatoxins can contaminate these food products during processing, storage, or transport when conditions are favorable for mold growth. NIEHS-funded scientists at the Massachusetts Institute of Technology were among the first to show that exposure to aflatoxin can lead to liver cancer. Their research also demonstrated that aflatoxin's cancer-causing potential is due to its ability to produce altered forms of DNA called adducts.

Researchers now use the levels of these DNA adducts in blood and urine as sensitive biomarkers of aflatoxin exposure in humans.

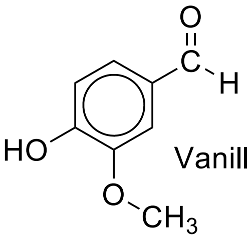
2 Coffee Chemistry: Coffee Aroma

(extracted from http://www.coffeeresearch.org/science/aromamain.htm)

Coffee aroma is responsible for all coffee flavour attributes other than the mouthfeel and sweet, salt, bitter, and sour taste attributes that are perceived by the tongue. Therefore, it might be said that coffee aroma is the most important attribute to specialty coffee.

The number of aromatic compounds found in coffee increases every year. Today the number is well over 800, and as our analytical methods become more precise, more will be uncovered.

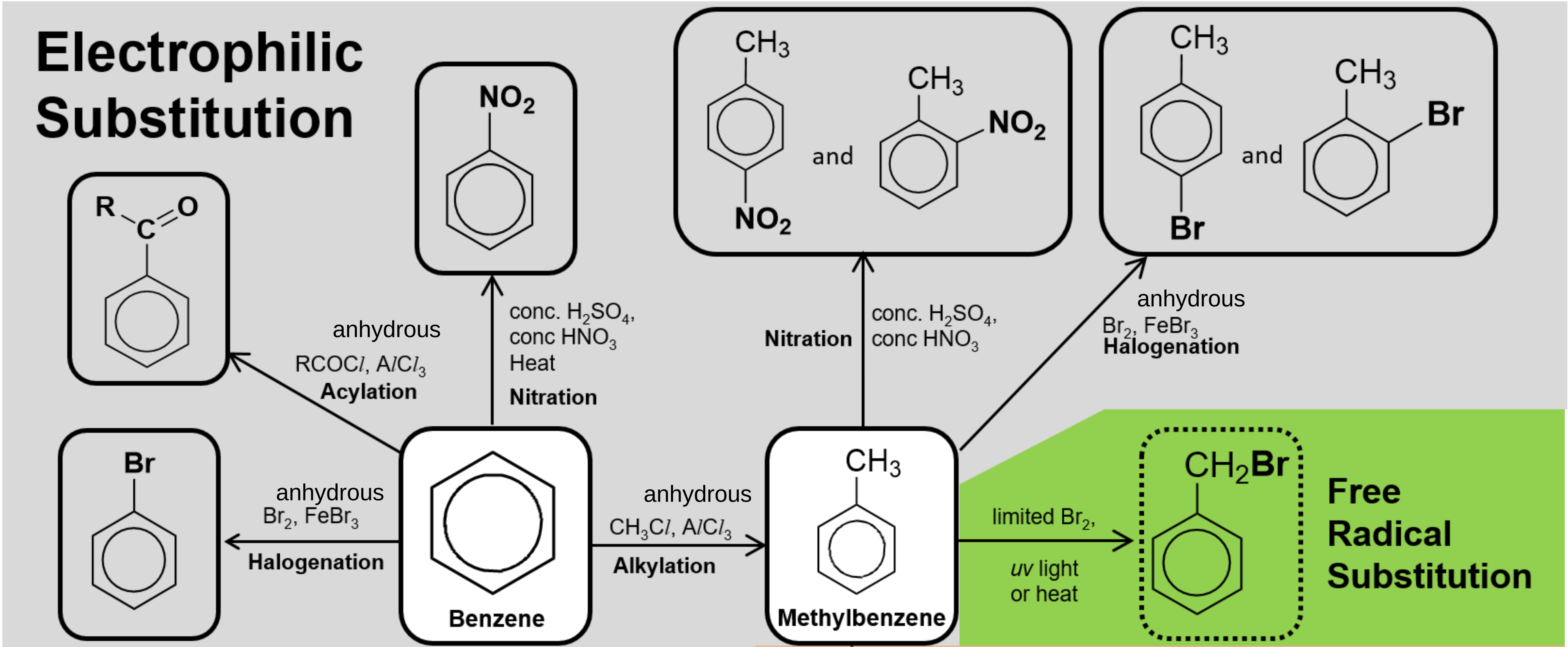
One of the simplest aromatic compounds that gives rise to the flavour and aroma of coffee is vanillin. Vanillin was first isolated from vanilla pods in 1858. By 1874 it had been obtained from glycosides of pine tree sap, temporarily causing an economic depression in the natural vanilla industry. By the late 19th century, semisynthetic vanillin derived from the eugenol found in clove oil was commercially available. In the 1930s, synthetic vanillin became significantly more available.



Vanillin

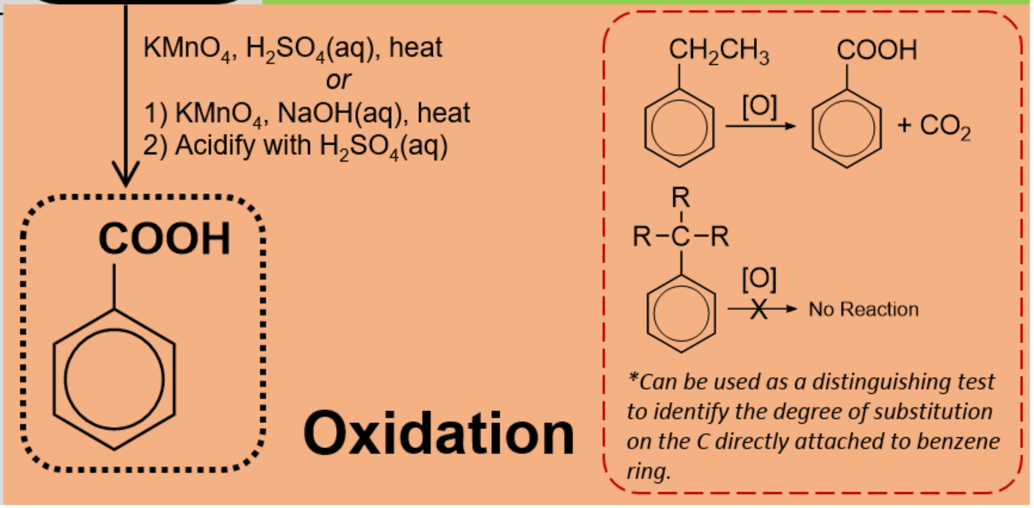
Besides coffee, vanillin is also widely used as a flavoring in sweet foods. The ice cream and chocolate industries together comprise 75% of the market for vanillin as a flavouring.

Vanillin is also a key ingredient in the perfume and pharmaceuticals industry. It is also used as a general purpose stain for the development of thin layer chromatography (TLC) plates for visualizing components of a reaction mixture as different range of colors.



Electrophilic Substitution

Free Radical Substitution



Oxidation

**Can be used as a distinguishing test to identify the degree of substitution on the C directly attached to benzene ring.*

Substituent Effect on Orientation of Electrophilic Substitution

2,4-directing	**Strongly Activating**	Amino groups($-NH_2$, $-NHR$) Hydroxyl($-OH$) or alkoxy groups ($-OR$)
	Weakly Activating	Alkyl groups ($-CH_3$)
	Weakly Deactivating	Halogen groups ($-Cl$, $-Br$)
3-directing	**Deactivating**	Nitro groups ($-NO_2$), Carbonyl groups ($-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-R$) Carboxyl groups ($-CO_2H$) Cyano groups ($-C{\equiv}N$)

5 Arenes Tutorial

Electrophilic Substitution

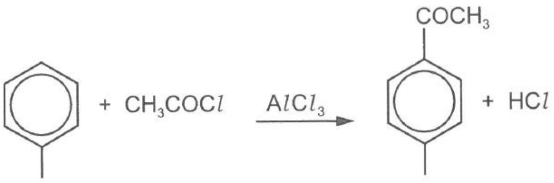
1 State the conditions used for the reactions of bromine with the following compounds and describe the mechanism of the reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

(a) ethene,

(b) benzene.

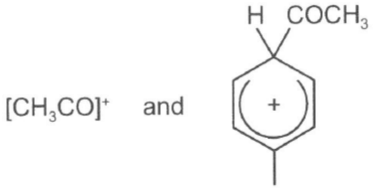
N2003/III/8a Either

2 (2019/p1/19) The reaction between methylbenzene and ethanoyl chloride is similar to the reaction between methylbenzene and chloroethane.

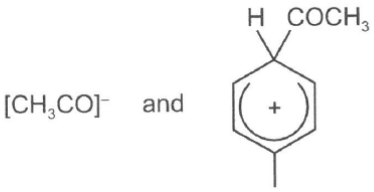


The reaction proceeds via several steps via two successive intermediates.
What could be the intermediates in this reaction.

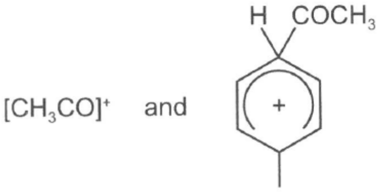
A



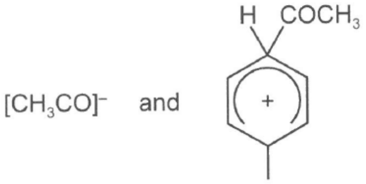
B



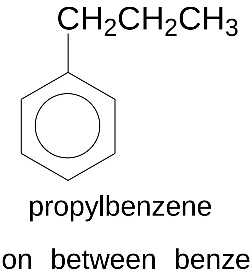
C



D



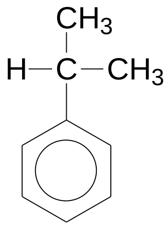
3 When 1-chloropropane, $CH_3CH_2CH_2Cl$ reacts with benzene in the presence of $AlCl_3$, under anhydrous condition, propylbenzene is obtained.



propylbenzene

(a) Outline the mechanism of the reaction between benzene and chloropropane to give propylbenzene as a product.

(b) Upon analysis of the reaction mixture, it is found that 1-methylethylbenzene is also formed in this reaction and has a greater abundance than propylbenzene.



1-methylethylbenzene

Give the structure of the electrophile that leads to the formation of 1-methylethylbenzene.

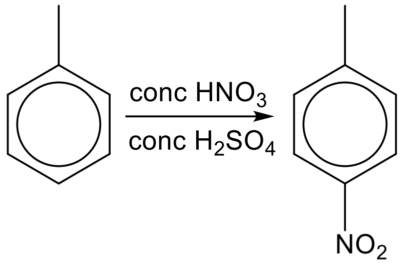
(c) Hence, explain why 1-methlyethylbenzene is formed in greater abundance. (You are not required to explain how the electrophile in part (b) is formed.)

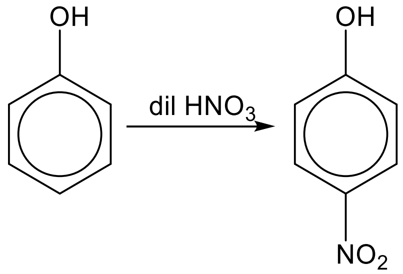
4 Rank the compounds in each group according to their reactivity towards electrophilic substitution.

(a) Phenylamine, bromobenzene, benzene

(b) Propylbenzene, 1,3-dimethylbenzene, nitrobenzene

5 Both methylbenzene and phenol react with nitric acid, but under different conditions.





(a) Explain why different conditions are needed for these two reactions.

(b) Describe the mechanism for nitration of methylbenzene to form 4-nitromethylbenzene.

(c) Nitration of phenol can produce 2-nitrophenol as well, which can be separated from 4-nitrophenol by steam distillation. Explain if 2-nitrophenol or 4-nitrophenol has a lower boiling point. (modified from N2009/III/5c)

Distinguishing Test

6 For each of the following pairs of compounds, describe one simple chemical test which would enable you to distinguish between them. State clearly the observations for each compound and write balanced equations for the reactions involved.

(a) cyclohexene and benzene

(b) benzene and methylbenzene

(c) methylbenzene and ethylbenzene

Application questions

7 Propose synthetic routes for the following. Give the reagents and conditions for each transformation step in the synthesis

(a) Benzene to 4-chloromethylbenzene

(b) Benzene to 3-methylbenzoic acid

(c) Methylbenzene to 3-nitrobenzoic acid

(d) Methylbenzene to 4-nitrobenzoic acid

8 A compound **P** (molecular formula C_8H_{10}) reacts with acidified potassium manganate(VII) under reflux to produce **Q,** $C_7H_6O_2$. When **P** is reacted with Cl_2 in the presence of $FeCl_3$ in the dark, two positional isomers, **R** and **S**, are formed. However, **P** reacts with limited Cl_2 under *uv* light to give another functional group isomer **T,** which has the molecular formula C_8H_9Cl**.** **T** reacts with ethanolic KOH under reflux to produce a hydrocarbon **U**.

Suggest structures for **P**, **Q**, **R**, **S**, **T** and **U** with reasons.

9 (2021/P3/4d) The position of substitution in the electrophilic substitution of mono-substituted arenes depends on the nature of the group P, already attached to the ring. This selectivity can be explained based on the stability of the intermediate formed in the first step. Fig. 1 Shows three possible first steps in the nitration of a mono-substituted arene and the products obtained.

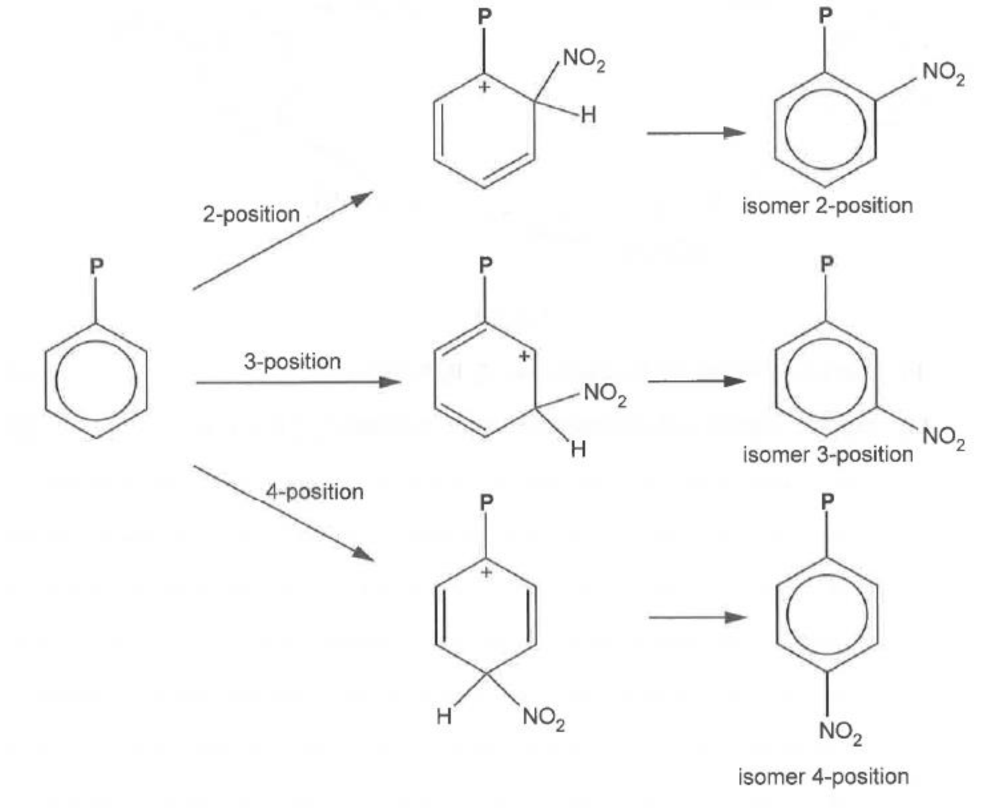


Fig. 1

Use this information to predict which substituted isomer in Fig 1. will be form the least and the most when P is a $(CH_3)_3C-$ group. Explain your reasoning.