Raffles Institution
Year 5 H2 Chemistry 2022
Lecture Notes 9 – Introduction to Organic Chemistry

Content

I. Empirical, molecular and structural formulae
II. Functional groups and the naming of organic compounds
III. Common terms for organic reactions and reactivities
IV. Shapes of organic molecules; σ and π bonds
V. Isomerism: *constitutional (structural); cis-trans; enantiomerism*

Learning Outcome
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.
(i) describe constitutional (structural) isomerism
(j) 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]
(k) explain what is meant by a chiral centre
(l) deduce whether a given molecule is chiral based on the presence or absence of chiral centres and/or a plane of symmetry
(m) recognise that an optically active sample rotates plane-polarised light and contains chiral molecules
(n) 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.]
(o) recognise that enantiomers have identical chemical properties except in their interactions with another chiral molecule
(p) recognise that different stereoisomers exhibit different biological properties, for example in drug action
(q) deduce the possible isomers for an organic molecule of known molecular formula
(r) identify chiral centres and/or *cis-trans* isomerism in a molecule of a given structural formula

Lecture Outline	**References**
1. Organic Chemistry and the Carbon Atom 2. Classification of Organic Compounds 3. Formulae of Organic Compounds 4. IUPAC Nomenclature for Organic Compounds 5. Isomerism 6. Terminology Associated with Organic Reactions	• Organic Chemistry as a Second Language by David Klein • Understanding Advanced Organic and Analytical Chemistry by Jeanne Tan & Kim Seng Chan • Organic Chemistry by Janice Smith • A-Level Chemistry by Peter Cann & Peter Hughes • Principles of Organic Chemistry by Peter R.S. Murray • An Introduction to Organic Chemistry by G.I. Brown • Chemistry in Context by Hill & Holman • http://www.chemguide.co.uk/orgmenu.html

1 Organic Chemistry and the Carbon Atom

1.1 Introduction

- Organic Chemistry is the chemistry of compounds that contain the element carbon (excluding those classified as inorganic compounds, such as CO, CO_2, bicarbonates, carbonates etc). Many such compounds are found in living plants and animals, and that is the origin of the term "organic".

- What are the common features of organic compounds?
  - All organic compounds contain carbon atoms and most contain hydrogen atoms.
  - All the carbon atoms have four bonds. A stable carbon atom is said to be tetravalent.
  - Other elements, such as N, O, S, P and the halogens, may also be present.
  - Some compounds have chains of atoms and some compounds have rings.

- There are three important properties of carbon that enable it to form so many stable compounds.
  - Carbon has a fully shared octet of electrons in its compounds.
  - Carbon can form strong single, double and triple bonds with itself, or any other groups of atoms.
  - Each carbon can form four covalent bonds, and thus a chain of carbon atoms can have many different groups attached to it and this leads to a wide diversity of compounds.

C

$1s^22s^22p^2$

- Organic compounds are relatively stable due to the
  - lack of lone pairs of electrons in the skeletal chains
  - inability of carbon to expand its valence shell to accommodate more than 8 electrons
  - presence of strong C–C and C–H bonds

1.2 Oxidation number of carbon in compounds

- Changes in the oxidation number of carbon in organic compounds indicate whether the compound has undergone an oxidation or a reduction reaction. Hence, we need to know how to determine the oxidation number of carbon from the structure of the organic compound.
  (refer to section 6.3 for the different types of reactions involving organic compounds)

- Recall from Topic 1b – Redox Reactions:
  - Oxidation number of atoms in an element = 0
  - In a compound, the more electronegative atom is given a negative oxidation number.
  - Sum of all oxidation numbers in a molecule = 0

- Examples of some common oxidation numbers

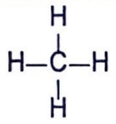
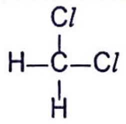
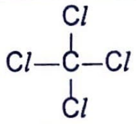
atom	O	H	F
oxidation number	−2 except in peroxides, e.g. H_2O_2	+1 except in metal hydrides, e.g. NaH	−1

How do we assign oxidation numbers from the structure of the compound?

- Bonding electrons are assigned to the more electronegative atom.
- Thus, for every bond, the
  - more electronegative atom "gains" an electron and the oxidation state decreases by 1.
  - less electronegative atom "loses" an electron and the oxidation state increases by 1.
- Note: Carbon is less electronegative than F, O, N, C*l*, Br, I and S.
  Carbon is slightly more electronegative than H.
- If a bond is formed between two atoms of the same element, both atoms have the same electronegativity, hence there is no "gain" or "loss" of electrons.
- This method is useful for any compound where an element occurs multiple times and would have different oxidation states.

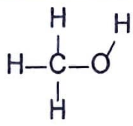
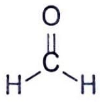
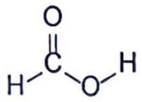
■■ Exercise 1 ■■

(a) State the oxidation number of carbon in each of the following compounds.

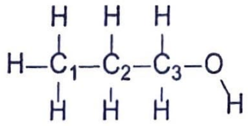
compound	methane, CH_4	dichloromethane, CH_2Cl_2	tetrachloromethane, CCl_4
structural formula	 $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}H}$	 $\mathrm{H{-}\overset{Cl}{\underset{H}{C}}{-}Cl}$	 $\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl}$
oxidation number of carbon	-4	0	+4

(b) (i) Determine the oxidation number of carbon in methanol, methanal and methanoic acid.
(ii) Hence, state the type of reaction undergone when methanol is converted to methanoic acid.

Type of reaction: oxidation

compound	methanol	methanal	methanoic acid
structural formula			
oxidation number of carbon	-2	0	+2

(c) Determine the oxidation number of all carbon atoms in the following compound.



oxidation number of

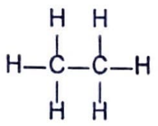
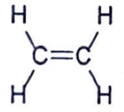
C_1: -3 C_2: -2 C_3: -1

1.3 Bonding and Shapes in Organic Molecules *(refer to topic on Chemical Bonding 2)*

Candidates should be able to:
☑ describe sp^3 hybridisation, as in ethane molecule, sp^2 hybridisation, as in ethene and benzene molecules, and sp hybridisation, as in ethyne molecule.
☑ explain the shapes of, and bond angles in, the ethane, ethene, benzene, and ethyne molecules in relation to σ and π carbon-carbon bonds.
☑ predict the shapes of, and bond angles in, molecules analogous to those specified above.

- Hybridisation helps to explain the
  - shape of the molecule
  - bond angles and bond lengths in the molecule

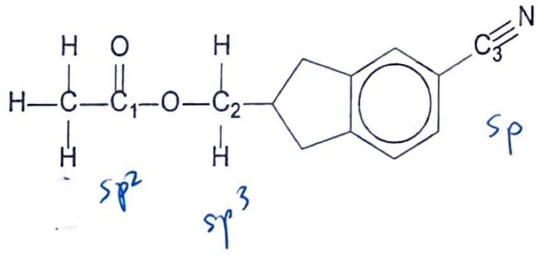
- In organic compounds, the carbon atom typically shows three types of hybridisation: sp, sp^2 and sp^3. Some examples are shown in the table below.

Compound	Type of hybridisation of each C atom	Type of carbon-carbon bond	Shape of molecule around each C atom	Bond angle / Number of σ and π bonds in each C atom
ethane  H_3C-CH_3	sp^3 (4 regions of electron density)	C—C	tetrahedral	109.5° / 4 σ bonds
ethene 	sp^2 (3 regions of electron density)	C=C (localised π bond)	trigonal planar	120° / 3 σ bonds and 1 π bond
benzene 		Resonance hybrid: C⩦C (delocalised π electrons) *(refer to topic on Arenes)*		120° / each C forms 3 σ bonds and has delocalisation of π electrons.
ethyne H—C≡C—H	sp (2 regions of electron density)	C≡C	linear	180° / 2 σ bonds and 2 π bonds

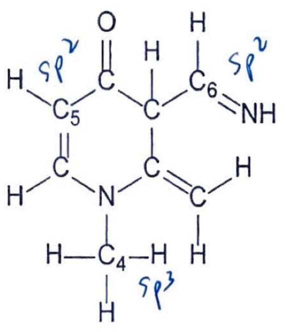
■■ Exercise 2 ■■

Label the hybridisation of each numbered C atom in the following compounds.

(a)



(b)



2 Classification of Organic Compounds

Candidates should be able to:

☑ Interpret and use the following terminology associated with organic reactions: functional group

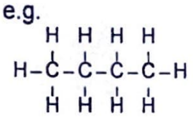
- Organic compounds can be classified based on the arrangement of the carbon skeleton:

HYDROCARBONS

Aliphatic hydrocarbons
- **open chains** of C atoms
- contain single or multiple C–C bonds

Straight chain hydrocarbons

e.g.



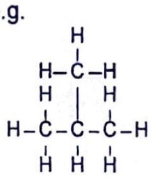
saturated

H—C≡C—H

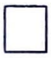
unsaturated

Branched chain hydrocarbons

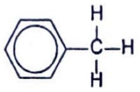
e.g.



Alicyclic hydrocarbons
- contain **closed ring** of C atoms
- contain single or multiple bonds
- H atoms are typically not shown in the structure

e.g.  is cyclobutane

Aromatic hydrocarbons
- contain benzene ring

e.g. 

- Since organic compounds may also contain elements other than carbon and hydrogen (e.g. N, O, S, P and the halogens), a more effective way of classifying them will be on the basis of functional group and homologous series.

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

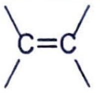
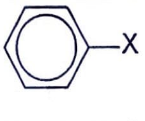
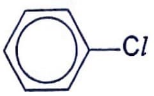
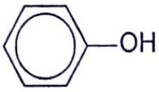
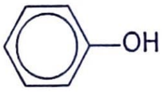
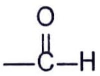
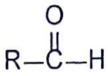
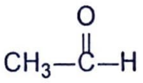
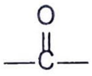
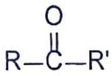
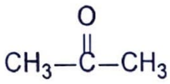
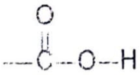
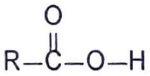
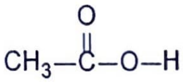
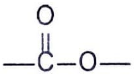
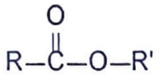
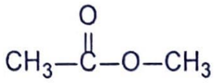
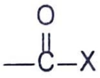
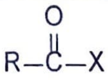
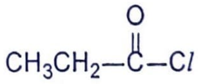
- A homologous series is a family of compounds having the same functional group. Homologues refer to the members in the same homologous series.

- Homologues have the following properties:
  - can be represented by a general formula
  - differs from the successive member by a methylene, $-CH_2-$, group
  - shows a gradual change in physical properties such as boiling points
  - have similar chemical properties
  - can be prepared by similar methods

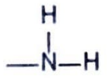
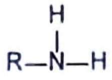
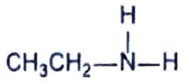
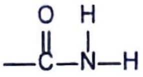
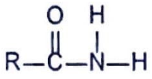
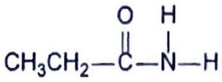
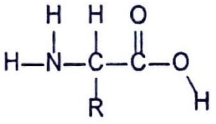
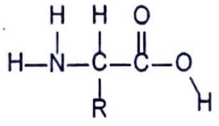
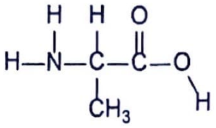
- The first and simplest homologous series: Alkanes (General Formula: C_nH_{2n+2})

molecular formula	structural formula	name	boiling point / °C
CH_4	CH_4	methane	–161
C_2H_6	CH_3CH_3	ethane	–89
C_3H_8	$CH_3CH_2CH_3$	propane	–44
C_4H_{10}	$CH_3(CH_2)_2CH_3$	butane	–0.5

- Some common homologous series and their respective functional groups are shown on the next two pages. (Note: Alkanes have no functional group)

Classes of compounds	Homologous series	Structure of functional group	General formula (R, R' = alkyl groups)*	Example
hydrocarbons	alkane	—	C_nH_{2n+2}	ethane CH_3CH_3
	alkene		C_nH_{2n}	ethene $CH_2{=}CH_2$
	alkyne	$-C{\equiv}C-$	C_nH_{2n-2}	ethyne $CH{\equiv}CH$
halogen derivatives	halogenoalkane	–X (X = Cl, Br, I)	RX (X = Cl, Br, I)	chloroethane $CH_3CH_2{-}Cl$
	halogenoarene	 (X = Cl, Br, I)	—	chlorobenzene 
hydroxy compounds	alcohol	–OH	R–OH	ethanol $CH_3CH_2{-}OH$
	phenol		—	phenol 
carbonyl compounds	aldehyde	 $-\overset{O}{\overset{\|}{C}}-H$	 $R-\overset{O}{\overset{\|}{C}}-H$	ethanal  $CH_3-\overset{O}{\overset{\|}{C}}-H$
	ketone	 $-\overset{O}{\overset{\|}{C}}-$	 $R-\overset{O}{\overset{\|}{C}}-R'$	propanone  $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$
carboxylic acids and derivatives	carboxylic acid	 $-\overset{O}{\overset{\|}{C}}-O-H$	 $R-\overset{O}{\overset{\|}{C}}-O-H$	ethanoic acid  $CH_3-\overset{O}{\overset{\|}{C}}-O-H$
	ester	 $-\overset{O}{\overset{\|}{C}}-O-$	 $R-\overset{O}{\overset{\|}{C}}-O-R'$	methyl ethanoate  $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$
	acyl halide (or acid halide)	 $-\overset{O}{\overset{\|}{C}}-X$ (X = Cl, Br, I)	 $R-\overset{O}{\overset{\|}{C}}-X$ (X = Cl, Br, I)	propanoyl chloride  $CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl$

*R and R' are known as alkyl groups with the general formula C_nH_{2n+1}. Examples are methyl (CH_3–), ethyl (CH_3CH_2–), propyl ($CH_3CH_2CH_2$–) etc.

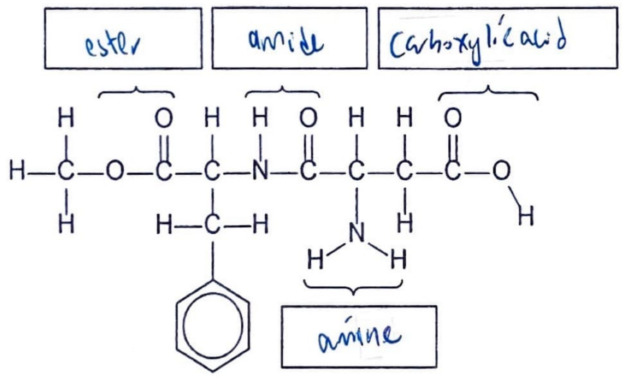
Classes of compounds	Homologous series	Structure of functional group	General formula (R, R' = alkyl groups)*	Example
nitrogen compounds	amine	 $-\overset{H}{N}-H$ (primary amine)	 $R-\overset{H}{N}-H$ (primary amine)	ethyl<u>amine</u>  $CH_3CH_2-\overset{H}{N}-H$
	amide	 $-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-H$ (primary amide)	 $R-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-H$ (primary amide)	propan<u>amide</u>  $CH_3CH_2-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-H$
	amino acid	 $H-\overset{H}{N}-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-H$	 $H-\overset{H}{N}-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-H$	alanine  $H-\overset{H}{N}-\underset{CH_3}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-H$
	nitrile	$-C\equiv N$	$R-C\equiv N$	propane<u>nitrile</u> $CH_3CH_2-C\equiv N$

*R and R' are known as alkyl groups with the general formula C_nH_{2n+1}. Examples are methyl (CH_3-), ethyl (CH_3CH_2-), propyl ($CH_3CH_2CH_2-$) etc.

■■ Exercise 3 ■■

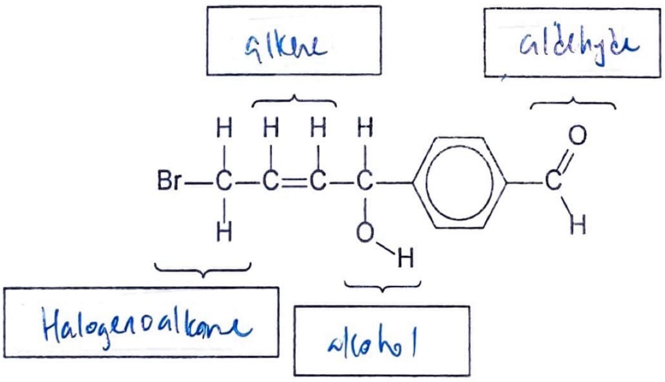
Identify the functional groups present in the following compounds.

(a)



Note: We usually do not label alkane and benzene functional groups.

(b)



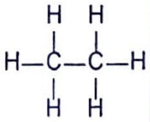
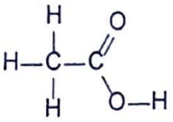
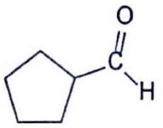
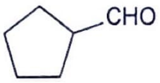
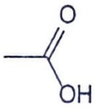
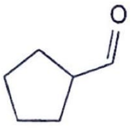
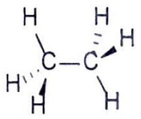
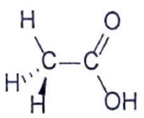
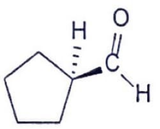
3 Formulae of Organic Compounds

Candidates should be able to:

- interpret and use the general formulae and displayed formulae of the following classes of compound: alkanes, alkenes and arenes, halogenoalkanes and halogenoarenes, alcohols and phenols, aldehydes and ketones, carboxylic acids, acyl chlorides and esters, amines, amides, amino acids and nitriles. *(Details will be covered in the respective functional group studies.)*

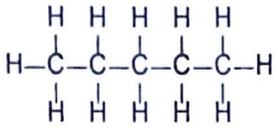
- Organic compounds can be represented by
  - Empirical formula
  - Molecular formula
  - Structural formula (displayed/full structural, condensed, skeletal and stereochemical)

- Unlike structural formula, empirical and molecular formulae usually do not show how the atoms are connected to one another.

Type of Formula		Characteristics	Examples		
			ethane	ethanoic acid	cyclopentane-carbaldehyde
Empirical		• Shows the simplest ratio of the different types of atoms in a molecule.	CH_3	CH_2O	$C_6H_{10}O$
Molecular		• Shows the actual number of each type of atom in a molecule. • Integral multiple (n) of empirical formula, e.g. $(CH_2O)_n$	C_2H_6	$C_2H_4O_2$	$C_6H_{10}O$
Structural	Displayed or Full structural	• Shows how every atom in the molecule is bonded to other atoms and the number of bonds between them. • C and H atoms in rings are not shown.			
	Condensed	• Shows how groups of atoms are sequentially arranged. • Bond lines are generally omitted (except for rings). • Read from left to right. • Parentheses are used around similar groups bonded to the same atom, e.g. $(CH_3)_3CH$	CH_3CH_3	CH_3CO_2H	
	Skeletal	• shows the carbon skeleton with any functional groups such as –OH or –Br. • Straight lines represent the C–C bonds. • There is a C atom at the junction of any two lines and at the end of any line. • H atoms attached to C atoms are not shown. • Number of H atoms bonded to each C atom can be inferred by the fact that each C atom must form 4 bonds.			
	Stereochemical	• Shows spatial 3D structure of a molecule. • Solid lines (——): Bonds on the same plane as the paper. • Dashed line (┄┄): Bonds receding into the paper. • Wedged line (◀—): Bonds coming out of the paper.			

How to draw skeletal structures

1. Carbon atoms in a straight chain are drawn in a zigzag format.

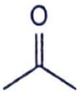


$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & H \\ & & | & & | & & | & & | & & | \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | \\ & & H & & H & & H & & H & & H \end{array}$$

is drawn as

2. When drawing double bonds or branched chains, draw all bonds as far apart as possible.

Draw



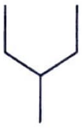
instead of

Draw

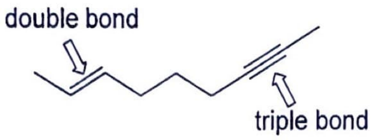
instead of

3. When drawing single bonds, the direction in which the bonds are drawn is irrelevant.

is the same as

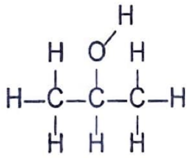


4. Double bonds are shown with two lines, and triple bonds are shown with three lines.



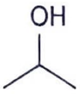
(Note: Triple bonds are drawn in a linear fashion rather than in a zigzag format as triple bonds involve sp-hybridised carbon atoms, which have a linear molecular shape.)

5. All heteroatoms (atoms other than carbon and hydrogen) are drawn, and any hydrogen atoms attached to a heteroatom is also drawn.

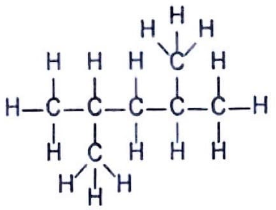
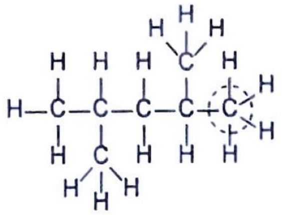
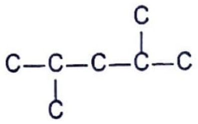


$$\begin{array}{ccccccc} & & & & H & & \\ & & H & & O & & H \\ & & | & & | & & | \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$$

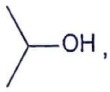
is drawn as



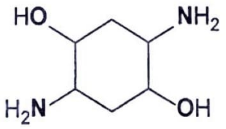
- The table below shows the structural formulae of 2,4-dimethylpentane and some mistakes to avoid.

☑ correct representations		☒ mistakes to avoid	
Displayed or Full structural formula			• Do not draw a C atom with more than 4 bonds. • The C atom (circled) has more than 4 bonds, which is not possible.
Condensed formula	$(CH_3)_2CHCH_2CH(CH_3)_2$	$(CH_3)_2\underline{\mathbf{C}}H_2CH_2\underline{\mathbf{C}}H_2(CH_3)_2$	• The C atoms (bold, underlined) have more than 4 bonds, which is not possible.
Skeletal formula			• Do not draw the C atoms without drawing the H atoms bonded to these C atoms.

- When drawing the structure of a molecule, ensure that the structure drawn is not ambiguous.

☑ correct representation	☒ mistake to avoid
$CH_3CH_2CH_2OH$	C_3H_7OH
Note: • C_3H_7- can either be $CH_3CH_2CH_2-$ or $(CH_3)_2CH-$ • Hence, the formula C_3H_7OH can either be  or , which is ambiguous.	

- When heteroatoms (atoms other than carbon and hydrogen) are bonded to a carbon skeleton, the heteroatom is joined directly to the carbon to which it is bonded, with no H atoms in between.



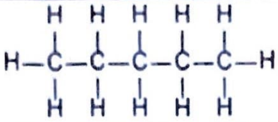
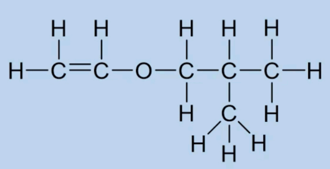
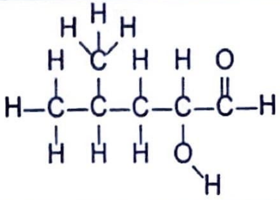
Place the **O** and **N** atoms directly bonded to the ring.

In contrast, when alkyl groups (e.g. $-CH_2CH_3$ group) are bonded to a carbon skeleton, the H atoms will be drawn to the right of the carbon to which they are bonded regardless of the location.

The C atoms (bold, underlined) are bonded to the ring

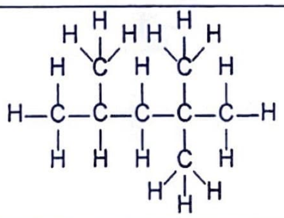
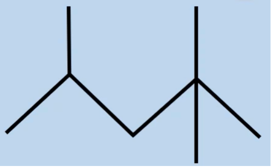
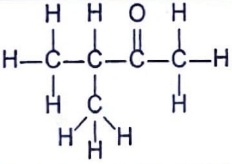
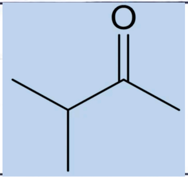
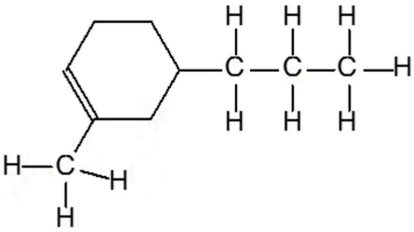
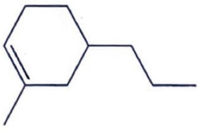
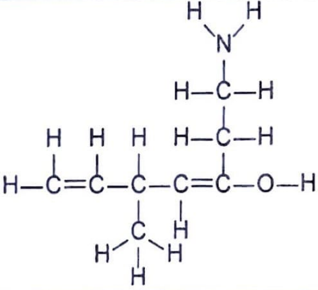
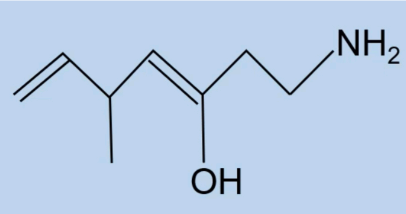
■■ Exercise 4 ■■

Draw the displayed or condensed formula of the compounds shown below.

Displayed Formula	Condensed Formula
	$CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$
	$CH_2CHOCH_2CH(CH_3)_2$
	$(CH_3)_2CHCH_2CH(OH)CHO$

■■ Exercise 5 ■■

Draw the displayed or skeletal formula of the compounds shown below.

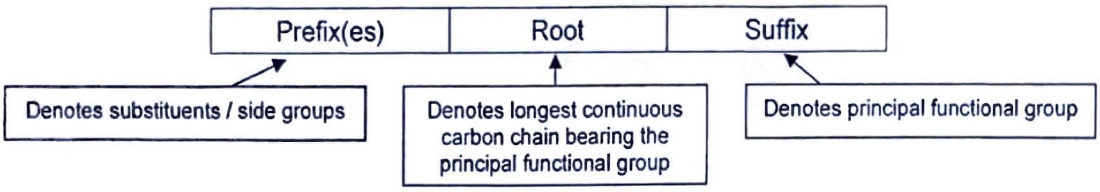
Displayed Formula	Skeletal Formula
	
	
	
	

4 IUPAC Nomenclature for Organic Compounds

(This will be covered in greater detail in future lectures on each functional group.)

Candidates should be able to:
☒ interpret and use the nomenclature of the following classes of compound: **alkanes, alkenes and arenes, halogenoalkanes and halogenoarenes, alcohols and phenols, aldehydes and ketones, carboxylic acids, acyl chlorides and esters, amines, amides, amino acids and nitriles.**

- The most common way to name organic compounds is to use the systematic naming developed by IUPAC (International Union of Pure & Applied Chemistry).
- Every name consists of a root, a suffix and one or more prefixes.



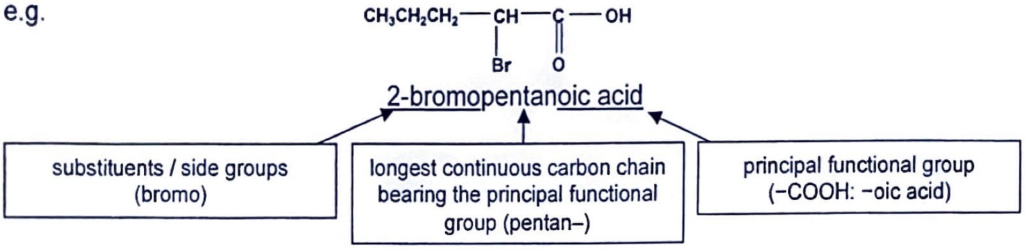
Prefix(es) | Root | Suffix

Denotes substituents / side groups

Denotes longest continuous carbon chain bearing the principal functional group

Denotes principal functional group

e.g.



$CH_3CH_2CH_2-\underset{Br}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-OH$

2-bromopentanoic acid

substituents / side groups (bromo)

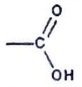
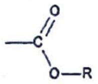
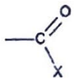
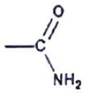
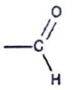
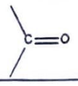
longest continuous carbon chain bearing the principal functional group (pentan–)

principal functional group (-COOH: -oic acid)

4.1 The Suffix

- Indicates the principal functional group that is present in the compound.
- The table below shows the principal functional groups listed in order of priority.

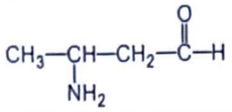
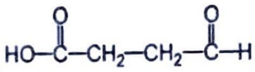
Order of increasing priority ↑

Formula of Functional Group	Functional Group	Suffix	Example
	carboxylic acid	**-oic acid**	CH_3**COOH** ethan**oic acid**
	ester	**alkyl.....oate**	$CH_3COOCH_2CH_3$ **ethyl** ethan**oate**
 (X= Cl, Br, I)	acyl halide (or acid halide)	**-oyl halide**	CH_3**COCl** ethan**oyl chloride**
	amide	**-amide**	$CH_3CH_2CH_2CONH_2$ butan**amide**
$-C{\equiv}N$	nitrile	**-nitrile**	CH_3CH_2CN propane**nitrile**
	aldehyde	**-al**	CH_3CHO ethan**al**
	ketone	**-one**	$CH_3CH_2COCH_3$ butan**one**
-OH	alcohol	**-ol**	CH_3CH_2OH ethan**ol**
$-NH_2$	amine	**-amine**	$CH_3CH_2CH_2NH_2$ propan**amine**

- Halogens (F, C*l*, Br, I) are usually not named in the suffix of a compound. Instead, they get named as substituents.

- When there are more than one functional group in the compound, the functional group higher in priority is listed as a suffix with everything else being a prefix.

Example:

compound	name	remarks
 $CH_3-\underset{NH_2}{CH}-CH_2-\overset{O}{C}-H$	3-aminobutanal	–CHO is higher in priority than –NH_2 so the suffix is –al, and –NH_2 is named as the prefix 'amino'.
 $HO-\overset{O}{C}-CH_2-CH_2-\overset{O}{C}-H$	4-oxobutanoic acid	–COOH is higher in priority than –CHO so the suffix is -oic acid, and –CHO is named as the prefix 'oxo'.

4.2 The Root

- In an aliphatic straight chain system, the name of the root takes its name according to the number of C atoms in the longest continuous chain bearing the principal functional group.

Number of carbon atoms	1	2	3	4	5	6	7	8	9	10
Root	meth-	eth-	prop-	but-	pent-	hex-	hept-	oct-	non-	dec-

- If a carbon-carbon multiple bond (e.g. C=C or C≡C) is also present, the longest possible chain will include both the principal functional group and carbon-carbon multiple bond.

- If there is no principal functional group present, the longest possible chain with carbon-carbon multiple bond (if any) will be chosen.

- In an alicyclic system, the word cyclo is added to the front of the root corresponding to the same number of C atoms.

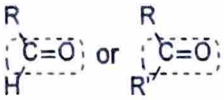
e.g. cyclopentane  cyclohexene 

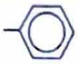
- For a saturated hydrocarbon, the name of the root ends with –an– (e.g. ethane).

- For an unsaturated hydrocarbon with
  - C=C bond ⇒ the name of the root ends with –en– (e.g. ethene).
  - C≡C bond ⇒ the name of the root ends with –yn– (e.g. ethyne).

4.3 The Prefix

- Denotes all other substituents on the longest continuous carbon chain bearing the principal functional group

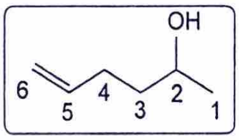
Substituent Group	Prefix
-C≡N	cyano-
	oxo-
-OH	hydroxy-
$-NH_2$	amino-
-OR	alkoxy-
-Br	bromo-
-Cl	chloro-
-F	fluoro-

Substituent Group	Prefix
-I	iodo-
$-NO_2$	nitro-
$-C_6H_5$ or 	phenyl-
$-CH_3$	methyl-
$-CH_2CH_3$	ethyl-
$-(CH_2)_2CH_3$	propyl-
$-(CH_2)_3CH_3$	butyl-
$-(CH_2)_4CH_3$	pentyl-
$-(CH_2)_5CH_3$	hexyl-

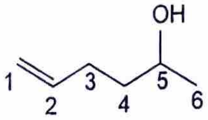
4.4 Positional Numbers

- Arabic numerals are used in the name to indicate the positions of attachment of substituents, carbon-carbon multiple bonds and/or principal functional group. These numbers are called positional numbers.

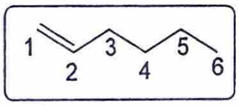
- The position of the principal functional group is denoted by the lowest carbon number possible.



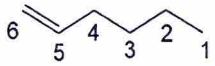
not



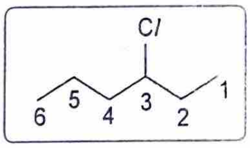
- If there is no principal functional group present, the carbon-carbon multiple bond (if any) gets the lowest carbon number possible.



not



- If there is no principal function group or carbon-carbon multiple bond, the position of the substituent is denoted by the lowest carbon number possible.



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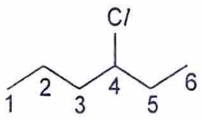
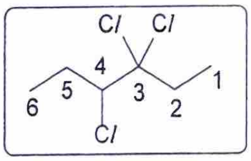


- If there is more than one substituent, the positions of the substituents are denoted by the lowest carbon number possible.



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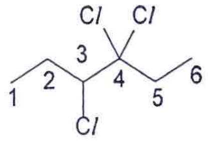
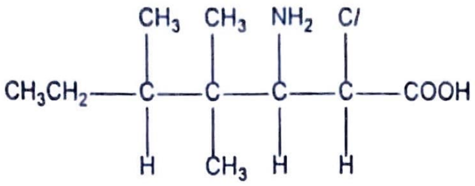
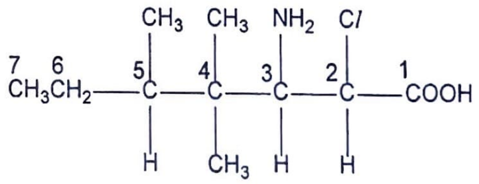


4.5 Steps to take in naming compounds

Example: Compound A $CH_3CH_2CH(CH_3)C(CH_3)_2CH(NH_2)CH(Cl)CO_2H$

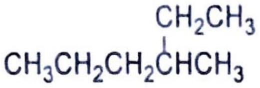
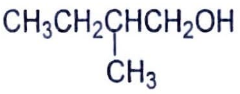
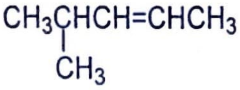
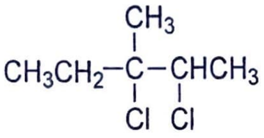
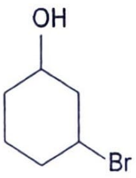
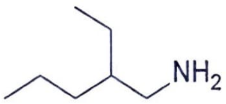
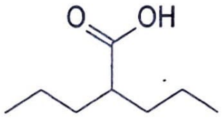
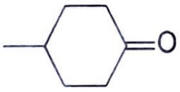


$CH_3CH_2-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{NH_2}{C}}-\underset{H}{\overset{Cl}{C}}-COOH$

Step 1: Suffix and Root (i) Identify the principal functional group (ii) Select the longest continuous C chain containing the principal functional group and carbon-carbon multiple bond (if any). Count the number of C atoms.	(i) principal functional group: $-CO_2H$ ⇒ suffix: '–oic acid' (ii) number of C atoms in longest chain: 7 ⇒ root: 'heptan–' (There are no carbon-carbon multiple bond in compound A)
Step 2: Prefixes Identify the prefixes (i.e. all remaining substituents).	other groups: $-CH_3$, $-NH_2$, $-Cl$ ⇒ prefixes: 'methyl', 'amino' and 'chloro'
Step 3: Positional Numbers Number the C atoms in the main chain from one end such that: (i) the lowest number is given to the group cited as the *suffix*, then (ii) the lowest possible individual numbers to the groups cited as *prefixes*.	(i) position of principal functional group: on C1 (ii) position of $-NH_2$: on C3 position of $-Cl$: on C2 position of $-CH_3$: two on C4 and one on C5
Step 4: String prefixes together • If same substituent appears more than once, indicate using di-, tri-, tetra- etc. • The appropriate positional number is still required even if the groups are connected to the same carbon on the main chain. • Different prefixes are listed in alphabetical order. Multiplying prefixes (e.g. di, tri) does not affect the alphabetical order. • Commas(,) are used to separate numbers, and hyphens(–) to separate numbers and words.	3-amino-2-chloro-4,4,5-trimethyl  $\overset{7\ 6}{CH_3CH_2}-\underset{H}{\overset{CH_3}{\overset{5}{C}}}-\underset{CH_3}{\overset{CH_3}{\overset{4}{C}}}-\underset{H}{\overset{NH_2}{\overset{3}{C}}}-\underset{H}{\overset{Cl}{\overset{2}{C}}}-\overset{1}{COOH}$
Step 5: String prefixes, root and suffix	IUPAC nomenclature for compound A is: 3-amino-2-chloro-4,4,5-trimethylheptanoic acid

■■ Exercise 6 ■■

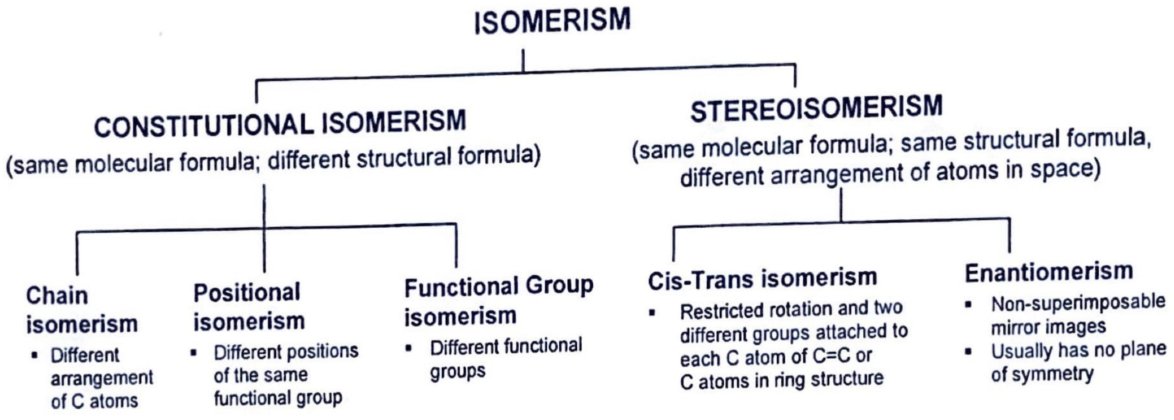
Write the IUPAC names of the following compounds.

Compound	IUPAC name
 $\mathrm{CH_3CH_2CH_2\overset{CH_2CH_3}{\overset{\vert}{C}}HCH_3}$	3-methyl hexane
 $\mathrm{CH_3CH_2\underset{CH_3}{\underset{\vert}{C}}HCH_2OH}$	2-methyl butan-1-ol
 $\mathrm{CH_3\underset{CH_3}{\underset{\vert}{C}}HCH{=}CHCH_3}$	4-methyl pent-2-ene
 $\mathrm{CH_3CH_2{-}\overset{CH_3}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}{-}\underset{Cl}{\underset{\vert}{C}}HCH_3}$	2,3-dichloro-3-methyl pentane
	3-bromocyclohexanol
	2-ethyl pentamine
	2-propyl pentanoic acid
	4-methyl cyclohexanone

5 Isomerism In Organic Compounds

Candidates should be able to:
☑ describe constitutional (structural) isomerism
☑ deduce the possible isomers for an organic molecule of known molecular formula

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



ISOMERISM

CONSTITUTIONAL ISOMERISM
(same molecular formula; different structural formula)

Chain isomerism
- Different arrangement of C atoms

Positional isomerism
- Different positions of the same functional group

Functional Group isomerism
- Different functional groups

STEREOISOMERISM
(same molecular formula; same structural formula, different arrangement of atoms in space)

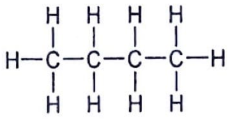
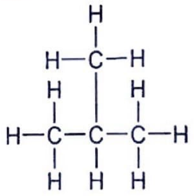
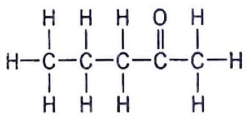
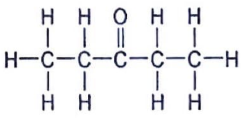
Cis-Trans isomerism
- Restricted rotation and two different groups attached to each C atom of C=C or C atoms in ring structure

Enantiomerism
- Non-superimposable mirror images
- Usually has no plane of symmetry

5.1 Constitutional (Structural) Isomerism

Constitutional (Structural) isomers have the same molecular formula but different structural formula, i.e. different arrangement of atoms.

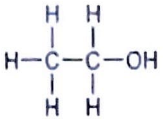
- There are three main types of constitutional (structural) isomers:

Constitutional (Structural) Isomers	Examples
Chain Isomers ▪ Differ in the arrangement of carbon atoms in the chain. Carbon atoms may be arranged in straight chain or branched chain. ▪ Same functional groups, thus similar chemical properties but different physical properties.	 butane C_4H_{10} (b.p. −0.5 °C)  2-methylpropane C_4H_{10} (b.p. −11.7 °C)
Positional Isomers ▪ Same homologous series with the functional group located at different positions on the same carbon skeleton. ▪ Same functional groups, thus similar chemical properties but different physical properties.	 pentan-2-one ($C_5H_{10}O$)  pentan-3-one ($C_5H_{10}O$)
Functional Group Isomers ▪ different functional groups, thus different chemical and physical properties.	See examples on the next page.

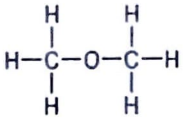
- Examples of functional group isomers:

- Alcohol and ether with general formula $C_nH_{2n+2}O$

e.g.



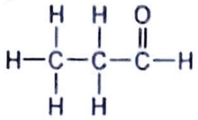
ethanol
C_2H_5OH
(b.p. 78.5 °C)



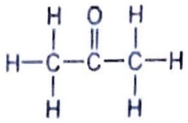
dimethylether
CH_3OCH_3
(b.p. –23 °C)

- Aldehyde and ketone with general formula $C_nH_{2n}O$

e.g.



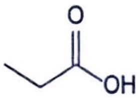
propanal
CH_3CH_2CHO
(b.p. 49 °C)



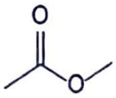
propanone
CH_3COCH_3
(b.p. 56.5 °C)

- Carboxylic acid and ester with general formula $C_nH_{2n}O_2$

e.g.



propanoic acid
C_2H_5COOH
(b.p. 141.2 °C)



methyl ethanoate
CH_3COOCH_3
(b.p. 57.1 °C)

- Alkene and cycloalkane with general formula C_nH_{2n}

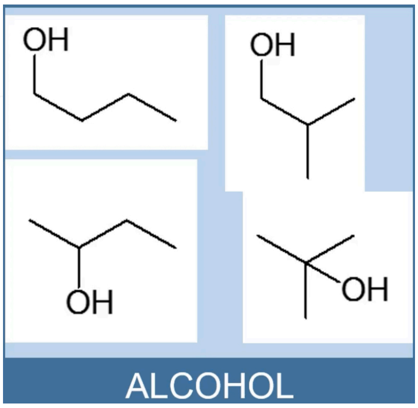
e.g.

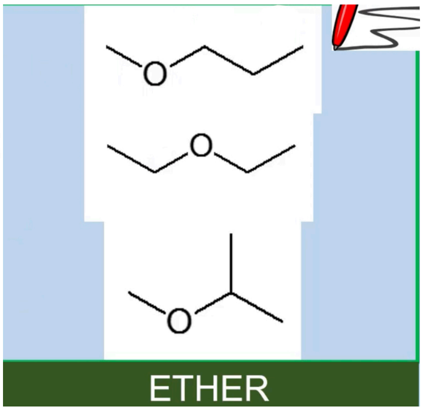
propene
CH_3CHCH_2
(b.p. –47.6 °C)

cyclopropane
C_3H_6
(b.p. –32.8 °C)

■■ Exercise 7 ■■

Draw all the constitutional isomers of the organic compounds with molecular formula, $C_4H_{10}O$.





Systematic way of drawing structural isomers:

1. Identify functional groups, e.g. alcohol and ether.
2. For one functional group, identify the longest chain, and draw all positional isomers.
3. Branch the chain and draw all positional isomers.
4. Repeat steps 2 and 3 for the other functional group.
5. Check that there are no repeating identical structures.

5.2 Stereoisomerism

Candidates should be able to:
- ☑ describe *cis-trans* isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds
- ☑ explain what is meant by a chiral centre
- ☑ deduce whether a given molecule is chiral based on the presence or absence of chiral centres and / or a plane of symmetry
- ☑ recognise that an optically active sample rotates plane-polarised light and contains chiral molecules
- ☑ recognise that enantiomers have identical physical properties except in the direction in which they rotate plane-polarised light
- ☑ recognise that enantiomers have identical chemical properties except in their interaction with another chiral molecule
- ☑ recognise that different stereoisomers exhibit different biological properties, for example in drug action
- ☑ identify chiral centres and/ or *cis-trans* isomerism in a molecule of a given structural formula

- Stereoisomerism refers to the existence of two or more compounds with the same molecular formula and structural formula but different spatial arrangement of atoms.

- There are two types of stereoisomerism:
  - Cis-trans Isomerism
  - Enantiomerism

5.2.1 Cis-Trans Isomerism

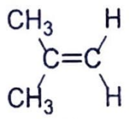
- The following 2 conditions must be met in order for cis-trans isomerism to exist:

1. Restricted rotation about a bond either by the presence of:
   - a double bond (C=C, C=N or N=N); or
   - a ring structure

2. For an alkene, each carbon atom in the C=C bond must have two different groups attached to it.

   For a cyclic compound, two or more of the carbon atoms in the ring must each have two different groups attached to them.

Example:



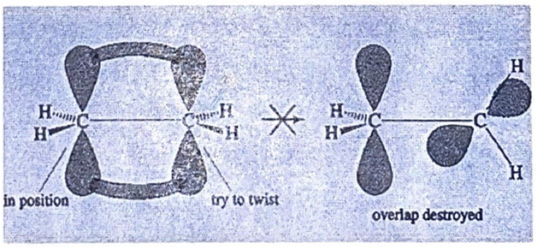
I

II

- Even though there is restricted rotation about the C=C bond in **I** and ring structure in **II**,
  - the C atoms of the C=C bond in **I** is bonded to two identical groups.
  - only one C atom in the ring in **II** has two different groups bonded to it.
- Hence, these two compounds do not exhibit cis-trans isomerism.

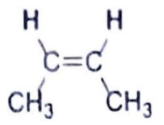
5.2.1 (A) Alkenes

- In alkenes, the C=C bond cannot undergo free rotation unless the π bond in the C=C bond is broken. Thus, there is restricted rotation across a C=C bond. (Note: There would also be restricted rotation across other double bonds such as N=N or C=N.)

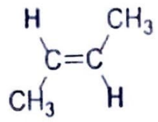


- If each carbon atom in the C=C bond has two different groups attached, two stereoisomers are possible:
  - A cis-isomer has the two identical groups on the same side of the C=C bond.
  - A trans-isomer has the two identical groups on the opposite sides of the C=C bond.

Example:



cis-isomer

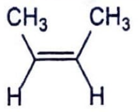
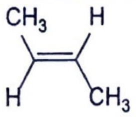


trans-isomer

- Since bond rotation cannot occur at the C=C bond, the two molecules cannot interconvert spontaneously, i.e. they are two distinct compounds.
- **Note:** When drawing cis-trans isomers, the trigonal planar geometry around each sp² C in the C=C bonds must be shown.

- If the number of such C=C bonds in a compound is n, the maximum number of cis-trans isomers for the compound is 2^n.

- Cis-trans isomers generally have similar (but not identical) chemical properties – they react with the same reagents, but at different rates. They have different physical properties, e.g:

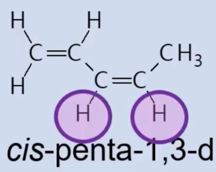
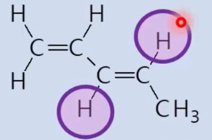
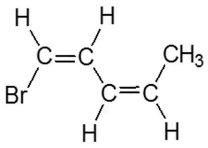
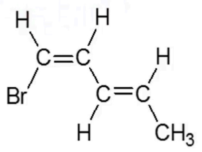
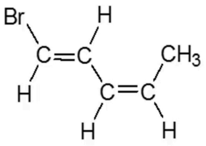
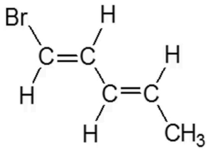
compound	*cis*–but-2-ene	*trans*–but-2-ene
structure		
boiling point / °C	3.72	0.88
melting point / °C	–138.9	–105.5

Compared to the trans-isomer, cis-isomer has a:

- higher boiling point because of its slightly higher polarity (the molecule has a very slight net dipole moment compared to the trans-isomer)
- lower melting point because it fits into a crystalline lattice more poorly.

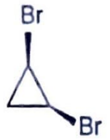
■■ Exercise 8 ■■

State the number of cis–trans isomers for the following compounds and draw these isomers.

Compound	penta-1,3-diene CH_2=CHCH=CHCH$_3$	1-bromopenta-1,3-diene BrCH=CHCH=CHCH$_3$
Number of C=C bonds that give rise to cis–trans isomerism	1	2
Number of cis–trans isomers	$2^1 = 2$	$2^2 = 4$
Structure of isomers	 *cis*-penta-1,3-diene  *trans*-penta-1,3-diene	 cis,cis-1-bromopenta-1,3-diene  cis,trans-1-bromopenta-1,3-diene  trans,cis-1-bromopenta-1,3-diene  trans,trans-1-bromopenta-1,3-diene

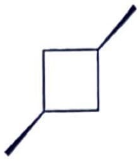
5.2.1 (B) Cyclic compounds

- As ring structures also prevent free rotation about a C–C bond, cis-trans isomerism is possible.
- Examples:

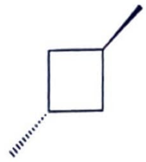


cis-1,2-dibromocyclopropane

trans-1,2-dibromocyclopropane



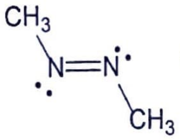
cis-1,3-dimethylcyclobutane



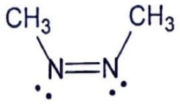
trans-1,3-dimethylcyclobutane

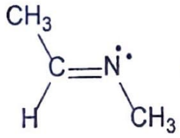
5.2.1 (C) Molecules with nitrogen-nitrogen (N=N) or carbon-nitrogen (C=N) double bond

- As there are also restricted rotation across other double bonds such as N=N or C=N, cis-trans isomerism is possible.
- Examples:

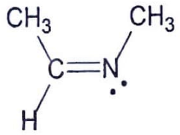


and





and



■■ Exercise 9 ■■

Which molecules have isomers that exhibit cis-trans isomerism? [N2005/I/21]

I	II	III	IV
C_3H_6BrI	C_3H_5I	$C_3H_4I_2$	C_3H_4BrI

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

B

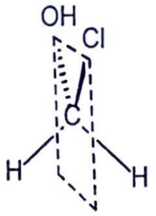
5.2.2 Enantiomerism *(or optical isomerism in the old A-level syllabus)*

- A compound displays enantiomerism if it forms a non-superimposable mirror image. Such compounds are also known as chiral compounds.

- Chiral compounds
  - do not have a plane of symmetry
  - usually contains one or more chiral centres

5.2.2 (A) Plane of Symmetry

- A molecule with a plane of symmetry forms a superimposable mirror image. It does not exhibit enantiomerism.
- Examples:

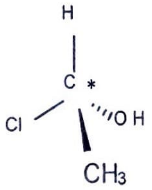


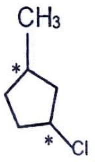
5.2.2 (B) Chiral Carbon (Carbon chiral centre)

- A chiral carbon is sp^3 hybridised and has four different groups attached to it.

- A molecule with no plane of symmetry and at least one chiral carbon forms non-superimposable mirror images. Such chiral molecules exhibit enantiomerism.

- Examples:

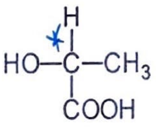




■■ Exercise 10 ■■

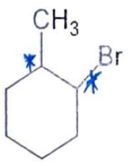
For the following compounds, mark the chiral carbon(s) with an asterisk (*).

(a)



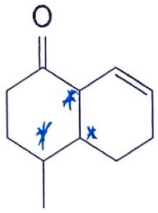
$$HO-\overset{\overset{H}{|}}{\underset{\underset{COOH}{|}}{C}}-CH_3$$

(b)



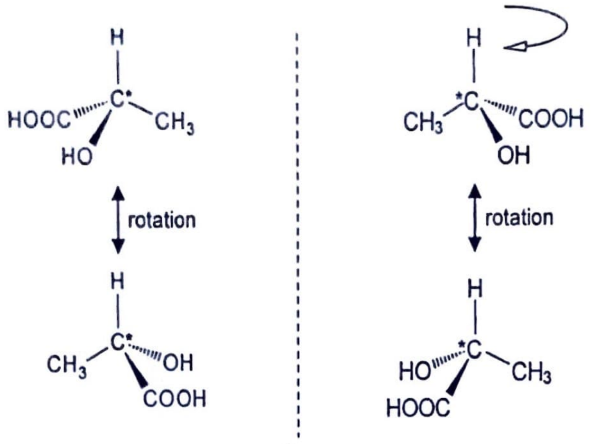
(c)

(d)



5.2.2 (C) Enantiomers

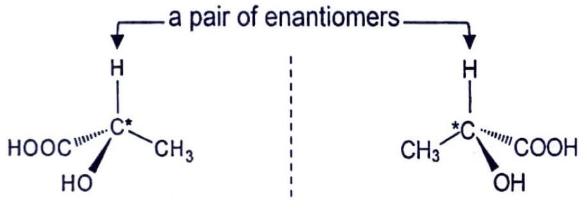
- Consider lactic acid, $CH_3CH(OH)COOH$, which has one chiral carbon and no plane of symmetry. Lactic acid is chiral and exhibit enantiomerism, i.e., it forms a non-superimposable mirror image.



(+)-Lactic acid | mirror plane | (-)-Lactic acid

Regardless of how you flip or rotate a molecule of (+)-Lactic acid, you will never be able to obtain the structure of a molecule of (-)-Lactic acid and vice versa.

- A pair of stereoisomers which are non-superimposable mirror images are also called enantiomers. The two enantiomers of lactic acid are two different compounds.



(+)-lactic acid | Mirror plane | (–)-lactic acid

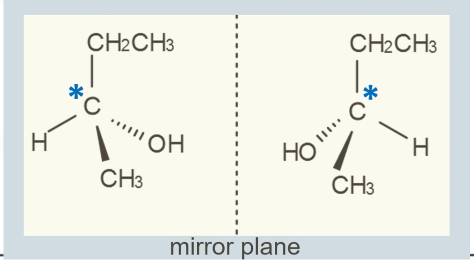
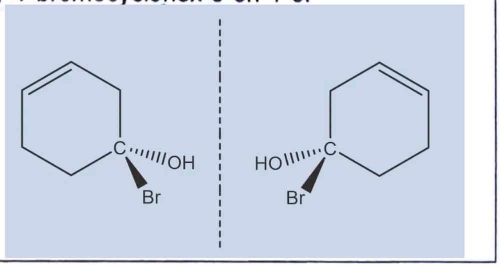
Note:
When drawing structures of enantiomers, use ‘▬’ and ‘┅’ to show the spatial 3-dimensional structure of a molecule.

- Compare and contrast the properties of the enantiomers:

Properties	Characteristics
Physical properties	Identical except that they rotate the plane of plane-polarised light in equal but opposite directions *(refer to 5.2.2.(D))*.
Chemical properties	Identical except in their interaction with another chiral molecule.
Biological properties	Different biological properties, e.g. drug action *(refer to pg 28)*

■■ Exercise 11 ■■

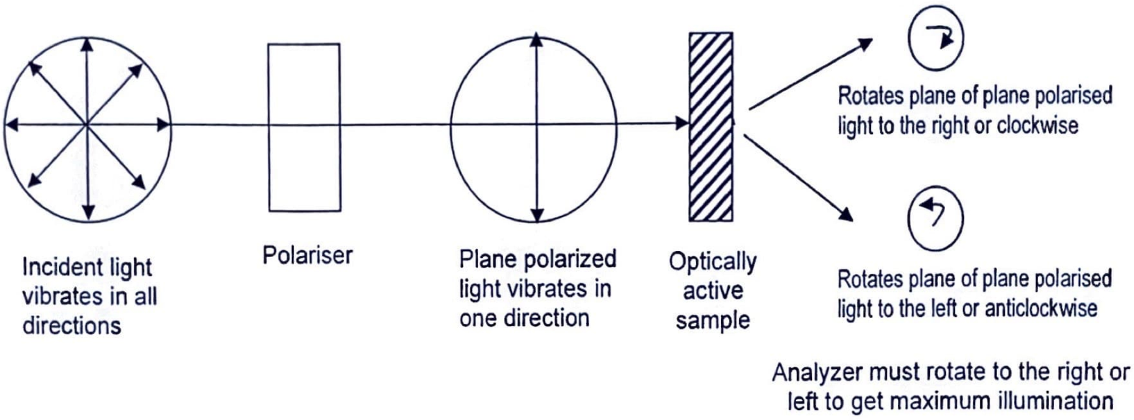
For each of the following compounds, draw the pair of enantiomers.

(a) butan-2-ol, $CH_3CH(OH)CH_2CH_3$	(b) 1-bromocyclohex-3-en-1-ol
	

5.2.2 (D) Rotation of plane-polarised light and optical activity

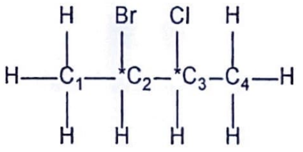
- Enantiomers differ in their rotation of the plane of plane-polarised light.

Samples containing:	Rotation of plane-polarised light	Optical Activity
(+)-lactic acid	▪ Rotates the plane of plane-polarised light clockwise	Optically active
(–)-lactic acid	▪ Rotates the plane of plane-polarised light by the same angle but anti-clockwise	Optically active
equal proportions of (+)-lactic acid and (–)-lactic acid (**racemic mixture**)	▪ The rotating power of one enantiomer exactly cancels that of the other. ▪ Does not rotate the plane of plane-polarised light.	Not optically active

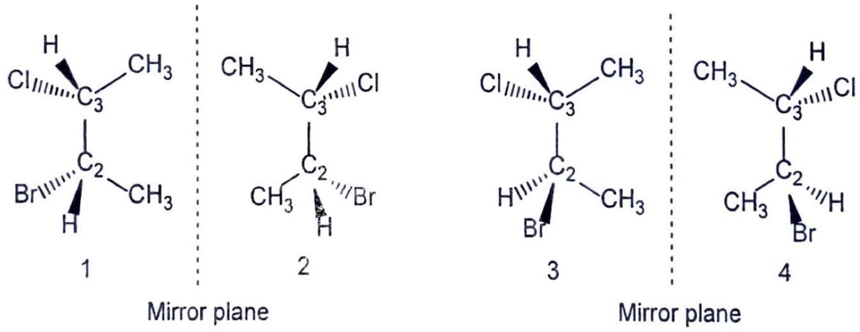


5.2.2 (E) Molecules with more than one chiral centres

- In general, a molecule with n chiral centers has a maximum of 2^n stereoisomers.
- Example: 2-bromo-3-chlorobutane has 2 chiral centers
  ⇒ Maximum number of stereoisomers = $2^2 = 4$



$$\mathrm{H-C_1H_2-{}^{*}C_2HBr-{}^{*}C_3HCl-C_4H_3}$$

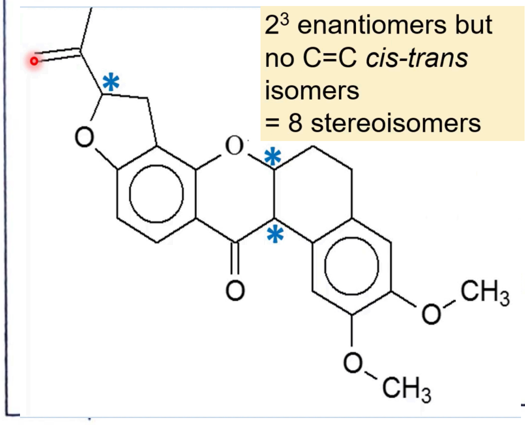
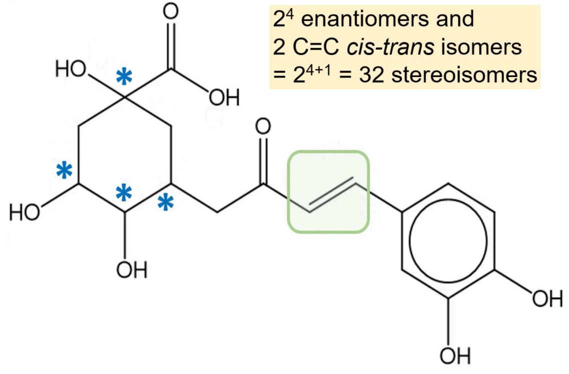


- Isomers 1 and 2 are non-superimposable mirror images of one another and so they are a pair of enantiomers.
- Isomers 3 and 4 are non-superimposable mirror images of one another and so they are a pair of enantiomers.
- Isomers 1 (or 2) and 3 (or 4) are stereoisomers which are not mirror images of one another. Stereoisomers which are not mirror images are called diastereomers.

Note: If a molecule has x chiral centres and y double bonds that give rise to cis-trans isomerism, the maximum number of stereoisomers it can form is $2^{(x+y)}$.

■■ Exercise 12 ■■

For the two molecules below, mark any chiral carbon(s) present with an asterisk (*) and state the number of stereoisomers each molecule can form.

(a) rotenone (an insecticide)	(b) Chlorogenic acid (occurs naturally in coffee and an edible species of bamboo)
 2^3 enantiomers but no C=C *cis-trans* isomers = 8 stereoisomers	 2^4 enantiomers and 2 C=C *cis-trans* isomers = 2^{4+1} = 32 stereoisomers

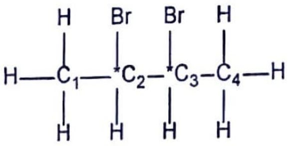
5.2.2. (F) Meso Compound

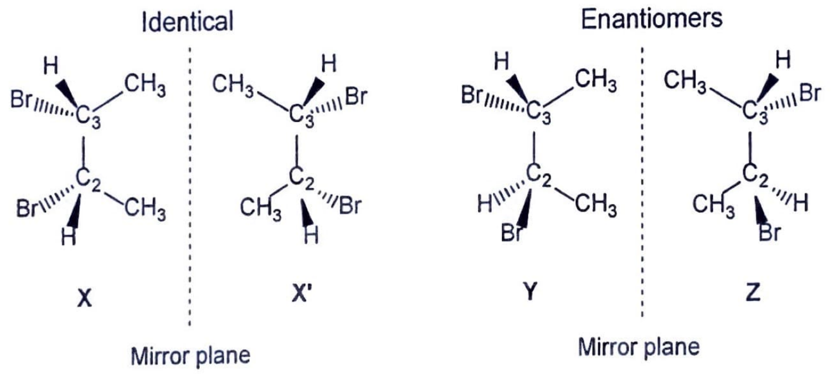
- A meso compound
    - contains more than one chiral centre but has a plane of symmetry
    - has mirror images that are superimposable
    - is optically inactive

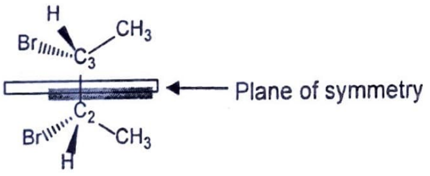
- Example:

  2,3-dibromobutane has 2 chiral centers but only 3 stereoisomers.

  Why is that so?



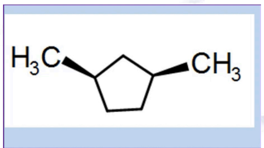




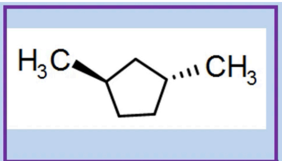
X and its mirror image, **X'**, are identical.
It is a **meso compound**.

■■ Exercise 13 ■■

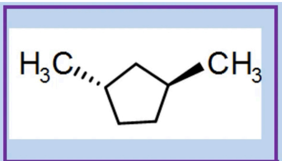
Draw the stereoisomers of 1,3-dimethylcyclopentane and determine if the stereoisomers are optically active.



NOT optically active



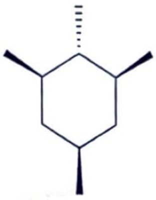
Optically active



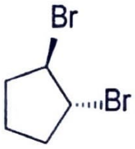
Optically active

■■ Exercise 14 ■■

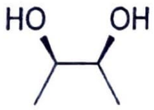
Determine if the following compounds are meso.



Yes



No



Yes

5.2.2 (G) Examples of the importance of enantiomerism in biological systems

- The small difference in the arrangement of atoms between the enantiomers may seem unimportant to you but to the cells of a living organism the difference is critical. Cells can recognise the difference and often can use only one of the enantiomer.

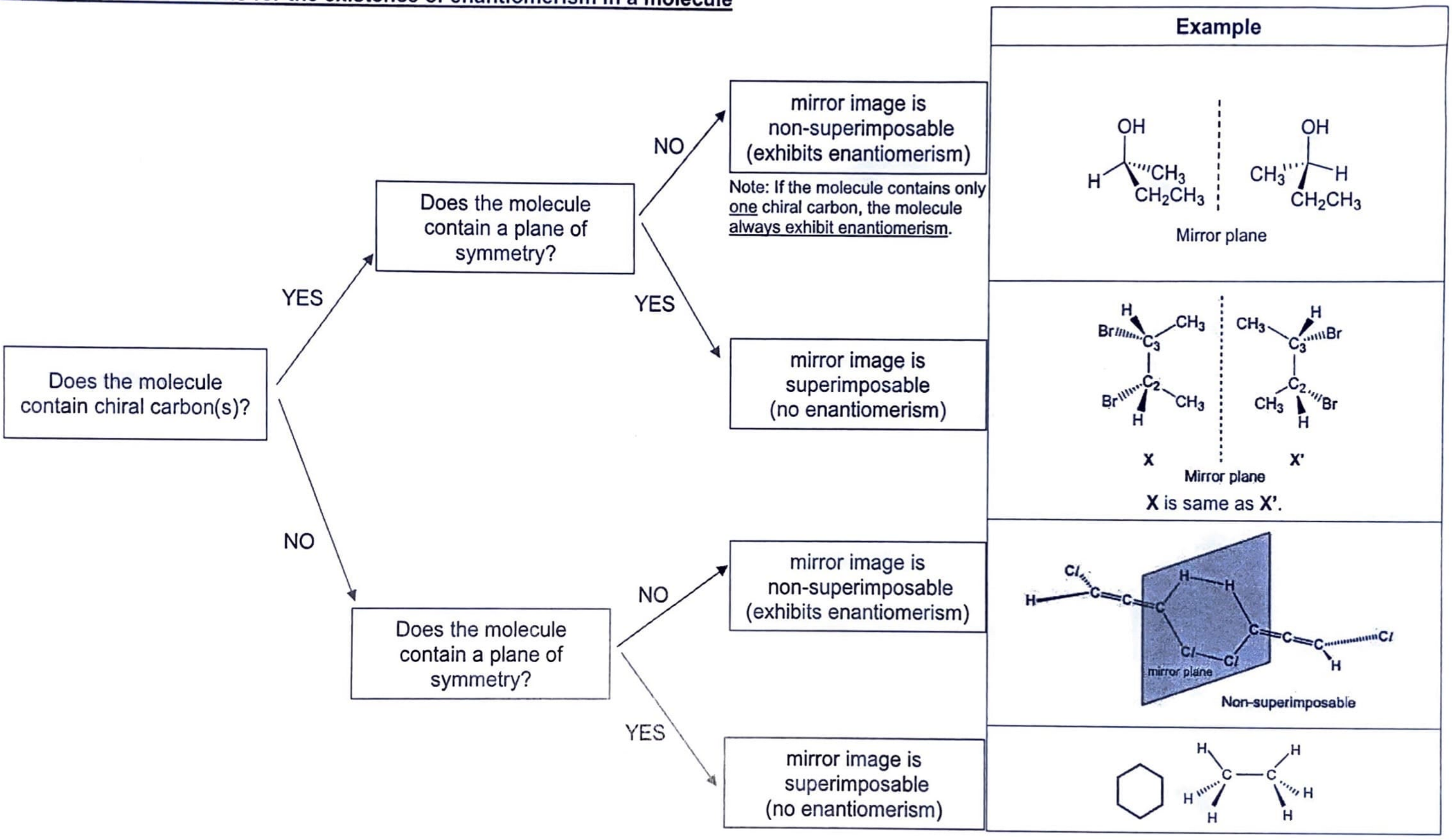
- Examples:
  - The proteins in our bodies are built up from only one enantiomer of each amino acid.
  - Enantiomers can interact differently with the chiral taste buds on your tongue to give different tastes.
  - Enantiomers can smell different. For instance, one enantiomer of limonene smells of oranges, the other of lemons.
  - Yeast can ferment only one enantiomer of glucose to produce alcohol but not the other.

- Different stereoisomers have different biological properties, e.g. in drug action. Very often, only one enantiomer of the drug works as a medicine, while the other form is useless or less effective or may even cause serious side effect.

- Examples:
  - One enantiomer of thalidomide has sedative properties while the other is a potent mutagen (it causes gene mutation which leads to deformed offspring). Read up more on the thalidomide disaster via the qr code.
  - One enantiomer of ethambutol fights tuberculosis, the other causes blindness.
  - Penicillin works by breaking peptide links which involve one enantiomer of alanine. These occur in the cell walls of bacteria but not in humans. When its cell wall is broken, the bacteria is killed. So penicillin is very effective in killing bacteria but cannot have the same effect on us because we do not use same enantiomer of alanine.
  - One enantiomer of ibuprofen is potent as a painkiller while the other is ineffective (and also harmless).
  - One enantiomer of DOPA is widely used for its potent activity against Parkinson's disease while the other has no biological effect.

- Hence, research is carried out to synthesise 'chiral drugs' that contain only one enantiomeric form. This is for protection against the possible side effects of its mirror image form.

Summary: Considerations for the existence of enantiomerism in a molecule



Note: If the molecule contains only one chiral carbon, the molecule always exhibit enantiomerism.

6 Terminology Associated with Organic Reactions

Candidates should be able to:

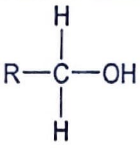
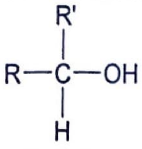
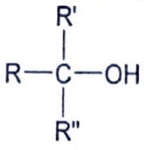
☑ interpret and use the following terminology associated with organic reactions: degree of substitution: primary, secondary, tertiary, quaternary, homolytic and heterolytic fission, carbocation, free radical, initiation, propagation, termination, electrophile (Lewis acid), nucleophile (Lewis base), addition, substitution, elimination, condensation, hydrolysis, oxidation and reduction. [In equations for organic redox reactions, the symbols **[O]** and **[H]** are acceptable.]

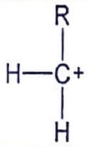
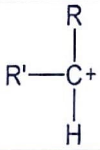
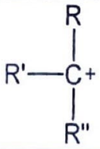
☑ recognise that the mechanisms of polar reactions involve the flow of electrons from electron-rich to electron poor sites.

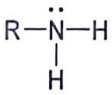
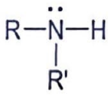
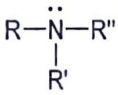
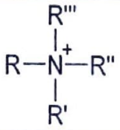
6.1 Degree of substitution

- The degree of substitution of an atom in an organic compound is determined by the number of alkyl or aryl groups bonded to it.

- Organic compounds with different degrees of substitution may undergo different reactions.

Type of alcohol	Primary (1°)	Secondary (2°)	Tertiary (3°)
Number of R groups bonded to carbon bearing the –OH group	1	2	3
Structure	 $R-\overset{H}{\underset{H}{C}}-OH$	 $R-\overset{R'}{\underset{H}{C}}-OH$	 $R-\overset{R'}{\underset{R''}{C}}-OH$

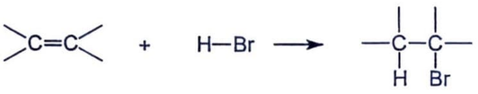
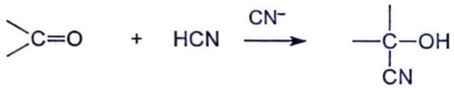
Type of carbocation	Primary (1°)	Secondary (2°)	Tertiary (3°)
Number of R groups bonded to carbon bearing the positive charge	1	2	3
Structure	 $H-\overset{R}{\underset{H}{C^+}}$	 $R'-\overset{R}{\underset{H}{C^+}}$	 $R'-\overset{R}{\underset{R''}{C^+}}$

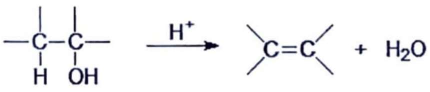
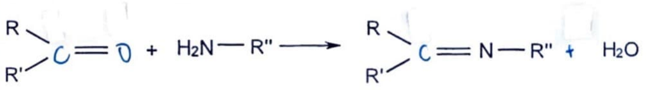
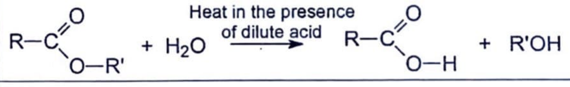
Type of amine	Primary (1°)	Secondary (2°)	Tertiary (3°)	Quaternary (4°)
Number of R groups bonded to nitrogen	1	2	3	4
Structure	 $R-\underset{H}{\ddot{N}}-H$	 $R-\underset{R'}{\ddot{N}}-H$	 $R-\underset{R'}{\ddot{N}}-R''$	 $R-\overset{R'''}{\underset{R'}{N^+}}-R''$

6.2 Types of organic species

Species	Defined as	Characteristics
Electrophile	Electron pair acceptor (Lewis acid)	• electron-deficient species (e.g. HBr, Br^+, NO_2^+) • attracted to regions of negative charge or regions of electron rich (δ–) sites in a molecule • may possess an empty low-lying/energetically accessible orbital to accept an electron pair
Nucleophile	Electron pair donor (Lewis base)	• electron-rich species (e.g. OH^-, CN^-, NH_3, H_2O) • attracted to regions of positive charge or regions of electron deficient (δ+) sites in a molecule • possess at least one lone pair of electrons
Free radical	An atom or group of atoms with an unpaired electron.	• contains an unpaired electron (e.g. Cl•) • electrically neutral

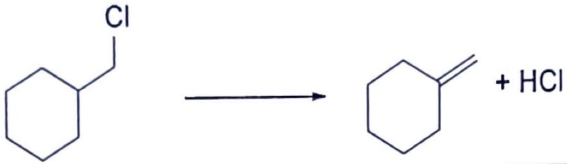
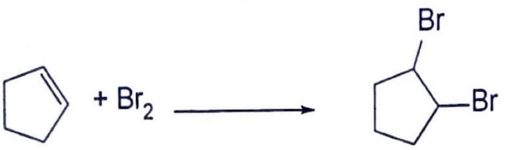
6.3 Types of organic reactions *(Details of the mechanisms will be covered in topics related to the functional groups.)*

	Types of reaction	Examples
Substitution - 1 atom or a group of atoms is replaced by another atom or group of atoms. - 2 species react to give 2 products. - A σ bond breaks and another σ bond forms at the same carbon atom. - Degree of unsaturation remains unchanged.	**Free Radical Substitution** ▪ in alkanes	$CH_4 + Cl_2 \xrightarrow{\text{uv light}} CH_3Cl + HCl$
	Electrophilic substitution ▪ in arenes	
	Nucleophilic substitution ▪ in halogenoalkanes	 $OH^- + -\overset{\vert}{\underset{\vert}{C}}-X \longrightarrow -\overset{\vert}{\underset{\vert}{C}}-OH + X^-$
Addition - Only occurs when there is unsaturation in the reactant molecules. - 2 species react to give a single product. - A π bond is broken to form two new σ bonds. - Decrease in degree of unsaturation.	**Electrophilic Addition** ▪ in alkenes	
	Nucleophilic Addition ▪ in aldehydes and ketones	

Types of reaction	Examples
Elimination • Involves removal of atoms or groups of atoms from adjacent carbon atoms to form multiple bonds. • 2 σ bonds are broken and a π bond is formed between adjacent atoms. • Degree of unsaturation increases.	
Condensation • Two molecules react together to form a bigger molecule with the elimination of small molecules such as H_2O or HCl. • Degree of unsaturation remains unchanged.	
Hydrolysis • A reaction in which water is used to break a bond in a molecule.	
Oxidation • the addition of oxygen; or • the removal of hydrogen from the molecule; or • loss of electrons; or • increase in oxidation number	$CH_3CHO + [O] \longrightarrow CH_3COOH$ [In equations for organic <u>oxidation</u> reactions, the symbol [O] is accepted.]
Reduction • the removal of oxygen; or • the addition of hydrogen to the molecule; or • gain of electrons; or • decrease in oxidation number	$CH_3CN + 4[H] \longrightarrow CH_3CH_2NH_2$ [In equations for organic <u>reduction</u> reactions, the symbol [H] is accepted.]
Rearrangement • Involves migration of an atom or groups of atoms from one site to another within the same molecule.	 $R-\underset{Cl}{CH}-CH=CH_2 \longrightarrow R-CH=CH-\underset{Cl}{CH_2}$

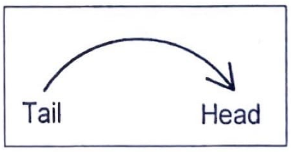
■■ **Exercise 15** ■■

For each of the following reactions, identify the type of reaction taking place.

		Type of Reaction
(a)		Substitution
(b)		Elimination.
(c)		Addition
(d)		Reduction
(e)		Oxidation

6.4 Mechanisms

- Organic reactions involve breaking and forming of covalent bonds.
- Every reaction involves the flow of electron density from electron–rich to electron–deficient sites. Electrons move when old bonds are broken and new bonds are formed.
- Mechanisms illustrate how the electrons move during a reaction. A proposed mechanism should be consistent with the reaction stoichiometry, the rate equation and with all other available experimental data.
- Curved arrows are used to show the movement of electrons.
  - o Tail: shows where the electrons are coming from (electron rich sites, e.g. bond pair, lone pair)
  - o Head: shows where the electrons are going to (i.e. electron-deficient sites)



6.5 Types of Bond Fission (Bond cleavage)

- There are 2 ways in which a covalent bond can break.

6.5.1 (A) Homolytic Fission

- The breaking of a covalent bond such that one electron goes to each of the atoms, forming free radicals.

$A{-}B \longrightarrow A\cdot + B\cdot$

(free radicals)

indicates the movement of one electron only

- Example:

$Cl{-}Cl \longrightarrow Cl\cdot + Cl\cdot$

6.5.1 (B) Heterolytic Fission

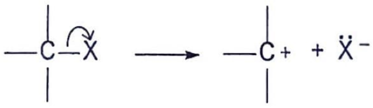
- The breaking of a covalent bond such that both electrons go to the same atom, typically forming positive and negative ions.

$A{-}B \longrightarrow \ddot{A}^- + B^+$

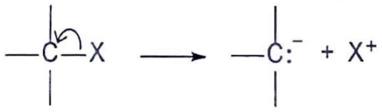
indicates the movement of a pair of electrons

- There are 2 ways how this can occur:

  (1) Both electrons go to the group that is bonded to the carbon atom. Often, this occurs when carbon is less electronegative than X. The positively charged carbon ion formed is called carbocation.



  (2) Both electrons go to the carbon atom. Often, this occurs when carbon is more electronegative than X. The negatively charged carbon ion formed is called carbanion.

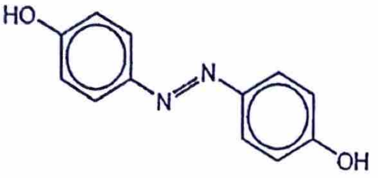


[More details on general mechanism drawing will be covered under the topic on Alkenes]

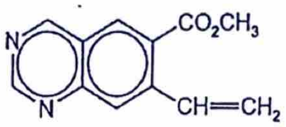
Raffles Institution
Year 5 H2 Chemistry 2022
Tutorial 9 – Introduction to Organic Chemistry

(A) Self-Check Questions

1 The three compounds X, Y and Z have the following structures.



X



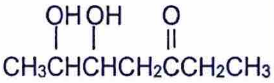
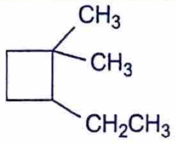
Y

Z

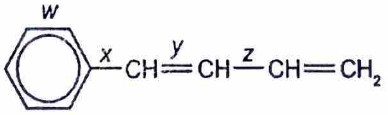
Which statements about X, Y and Z are correct?

1 X and Z have the same empirical formula.
2 X and Y are isomers.
3 The M_r of Y is exactly twice that of Z. *(N2011/I/33)*

2 Give the IUPAC names of the following compounds.

	(a)	**(b)**	**(c)**
	$CH_2{=}CHCH(Cl)CH_2CH_3$	 $CH_3\overset{OH}{\overset{\vert}{C}}H\overset{OH}{\overset{\vert}{C}}HCH_2\overset{O}{\overset{\Vert}{C}}CH_2CH_3$	
IUPAC name			

3 Four carbon-carbon bonds are labelled in the diagram.



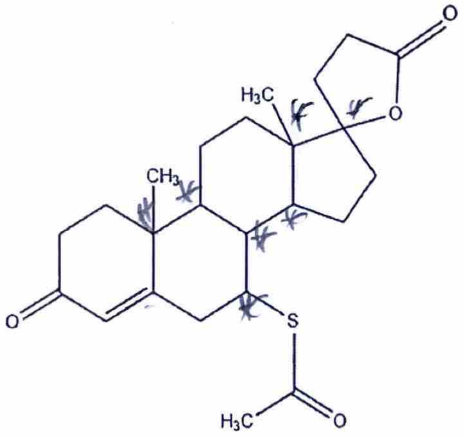
Which bonds are made up of an sp^2–sp^2 overlap?

A w and y only **B** w, x and y only **C** x, y and z only **D** w, x, y and z

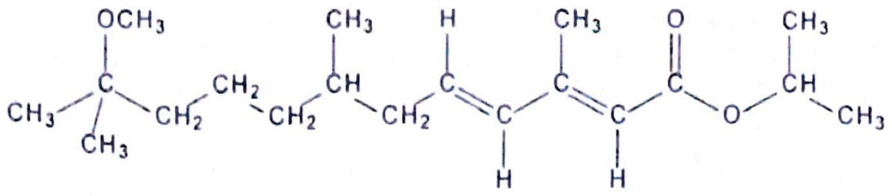
4 Spironolactone (structure shown on the right) is an anti–androgen used as a component in hormone therapy.

How many stereoisomers does spironolactone have?

A 2^3
B 2^4
C 2^6
D 2^7



5 The diagram shows the structure of the insect attractant methoprene.



What is the total number of stereoisomers (*cis-trans* isomers and enantiomers) of this molecule?

A 3 **B** 4 **C** 8 **D** 16

Discussion Questions

6 Draw the structural formulae for all the compounds having the formula C_5H_{10}.

Identify the compounds which are:

- constitutional isomers
- cis-trans isomers
- enantiomers

(There are a total of 6 alkenes and 7 cycloalkanes, including stereoisomers.)

7 Draw the displayed formulae of the following compounds.

(a) 3-phenylbutan-2-ol	**(b)** 2-aminopentanedial	**(c)** 1,3-dimethylcyclohexene

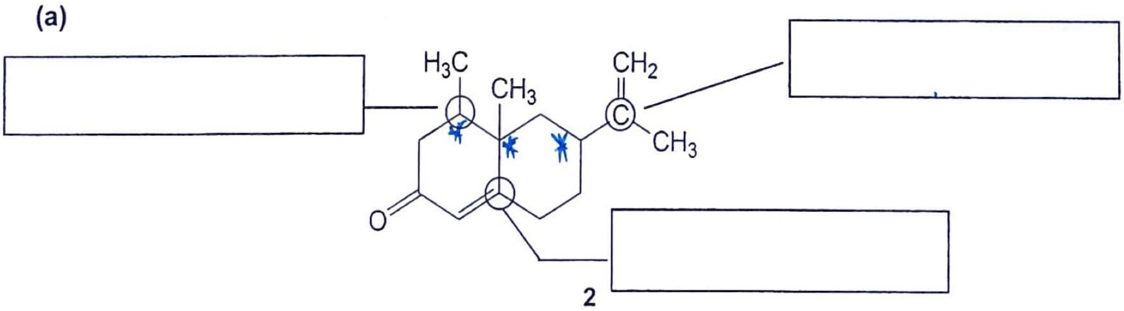
8 Draw the skeletal formulae of the following compounds.

(a) 2,2-dimethylpropane	**(b)** (1-chloroethyl)cyclohexane	**(c)** 3-oxobutanoic acid

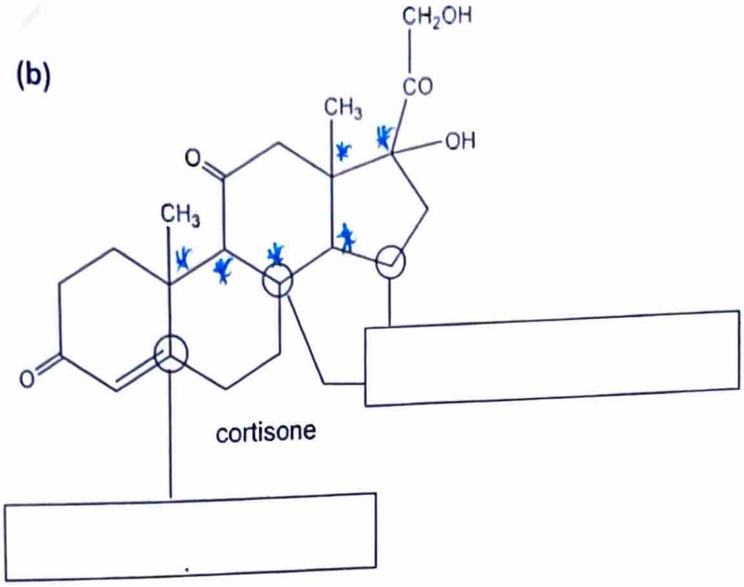
9 For each of the following compounds,

(i) state the hybridisation and the geometry of each circled carbon atom in the boxes provided
(ii) mark any chiral carbons present with an asterisk (*)

(a)

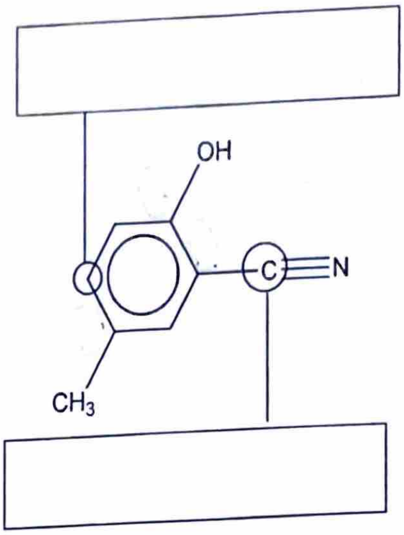


(b)



cortisone

(c)

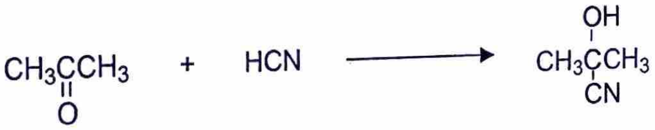


10 Classify each of the following reactions as addition, substitution, elimination, hydrolysis, reduction, condensation or rearrangement.

(a)

(b) $CH_2{=}CH_2 + H_2 \longrightarrow CH_3CH_3$

(c)



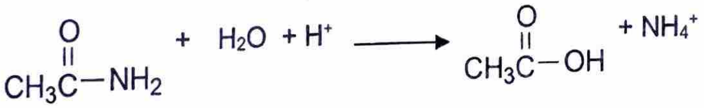
$$CH_3\underset{\underset{O}{\|}}{C}CH_3 + HCN \longrightarrow CH_3\overset{OH}{\underset{CN}{C}}CH_3$$

(d) $CH_3CH_2CH_2Cl \longrightarrow CH_3CH{=}CH_2 + HCl$

(e) $CH_3CH_3 + Cl_2 \longrightarrow CH_3CH_2Cl + HCl$

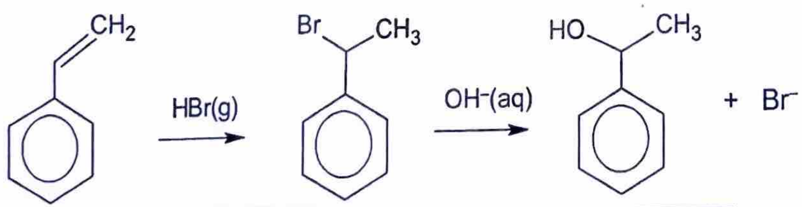
(f) $CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O$

(g)



$$CH_3\overset{\overset{O}{\|}}{C}{-}NH_2 + H_2O + H^+ \longrightarrow CH_3\overset{\overset{O}{\|}}{C}{-}OH + NH_4^+$$

(h)



step 1

step 2

11 Linoleic acid is an essential fatty acid in human diet and its structural formula is given below.

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

In linoleic acid, both C=C bonds are in the *cis* configuration.

By representing the structure as **A-CH=CH-CH$_2$-CH=CH-B**, draw the displayed formulae of linoleic acid and its *cis-trans* isomers in the boxes provided, showing clearly the configuration of the C=C bonds.

linoleic acid (*cis,cis*-isomer)	*trans,cis*-isomer
cis,trans-isomer	*trans,trans*-isomer

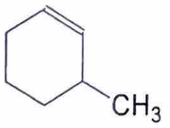
12(a) What do you understand by the terms *cis-trans isomerism* and *enantiomerism*? What are the criteria for a molecule to exhibit each of type of stereoisomerism?

(b) State and explain clearly which, if any, of these types of stereoisomerism would be shown by each of the following compounds. For compounds which show stereoisomerism, draw the structures of all the stereoisomers and mark any chiral carbons with an asterisk (*).

(i) hex-3-ene, $CH_3CH_2CH{=}CHCH_2CH_3$

Type(s) of stereoisomerism: ____________________ No. of stereoisomers: _____

(ii) 3-methylcyclohexene,



Type(s) of stereoisomerism: ____________________ No. of stereoisomers: _____

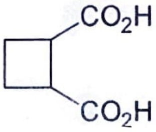
(iii) $CH_3CH=CHCH_2CH(OH)CH_3$

Type(s) of stereoisomerism: ______________________ No. of stereoisomers: ______

(iv) $(CH_3)_2C=CHCH_2CH(OH)CH_2CH=C(CH_3)_2$

Type(s) of stereoisomerism: ______________________ No. of stereoisomers: ______

(v) cyclobutane-1,2-dicarboxylic acid,



Type(s) of isomerism: ______________________ No. of stereoisomers: ______