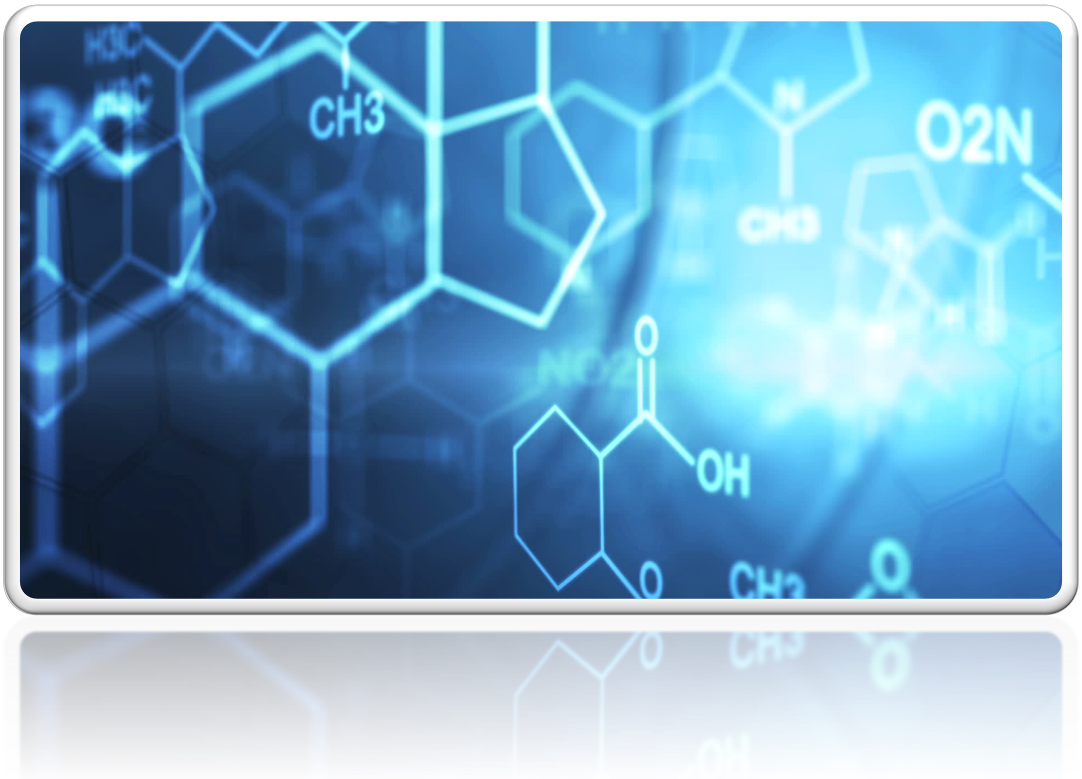
Organic Chemistry



Topics covered in this chapter:

4.1 Introduction to Bonding and Terminology

- Carbon has 4 electrons in its outer shell and needs to form four covalent bonds in order to be stable.

- This can be achieved in one of three ways:
  - Four single covalent bonds with a tetrahedral structure as the basic shape.
  - One double bond and two single bonds with a triangular planar structure as the basic shape.
  - One triple bond and one single bond with a linear structure as the basic shape.

Hint:

- Carbon often forms single bonds with other carbon atoms, hydrogen, oxygen, nitrogen and the halogens.
- Carbon often forms double bonds with other carbon atoms and oxygen.
- Carbon often forms tripe binds with other carbon atoms and nitrogen.

Functional Groups

These are the chemically reactive part of an organic molecule. Some important functional groups are:

Functional Group	Structure	Prefix/Suffix
Alkenes		-ene
Alcohols		-ol
Aldehydes		-al
Ketones		-one
Carboxylic Acid		-oic acids
Esters		-yl -oate
Amides		-amide
Amines		-amine

IUPAC rule for naming organic molecules

- Identify the functional groups in the molecule and determine which group has the highest priority in naming.
- Select the longest continuous carbon chain containing the highest priority functional group.
- Number the chain from the end which gives the main functional group with the lowest number.
- Use the appropriate prefix or suffix to name each functional group.
- Alphabetical order is used when more than once group is involved.
- Numbers are separated from words by a hyphen (-) and from other numerals by comma.

When naming molecules that have more one of a functional group attached the following prefixes are used:

2	3	4	5	6	7	8	9	10
di	tri	tetra	penta	hexa	hepta	octa	nona	deca

Worked Example

Draw the structural formula for 3,4-dimethylhexane

4.1 Summary Questions

Question 1.

Name the following compounds:

Question 2:
Name the following compounds:

Question 3
Draw the structural formulae for the following compounds

(a). 3,4-diethyloctance

(b) 1,3,4-triiodohexane

(c) 1,1-dichloropent-2-ene

(d) 3,6-diethylnon-4-ene

Question 4

Identify what is **incorrect** about the name of each of the following.

(a). but-3-ene

(b). 2-ethylprop-1-ene

(c). pent-4-ene

(d). 3,4-dimethypent-4-ene

4.2 Isomerism

Structural Isomers

- Structural isomers are molecules that have the same molecular formula but have different properties.
- They have different chemical and physical properties because they have different arrangements of the atoms in the the molecules, i.e. they have different structures.

Some examples of structural isomers

Molecular formula: C_5H_{10}

Cis and trans isomers

- Cis and trans isomers only occur in alkenes.
- The existence of the double bond restricts rotation and so the molecule with the same structural formula can have different geometries and hence different properties.
- The cis prefix refers to the different structures being on the same side
- The trans prefix refers to the different structures being on different sides of the double bond.

Worked Example:

Name the following cis/trans isomers:

4.2 Summary Questions

Question 1

Name the following compounds using the prefix "cis" and "trans"

Question 2

Draw the cis and trans isomers for each of the following (if the isomers exist).

(a). hept-1-ene

(b) 1,2-dichloroethene

(c) 1-chloropent-1-ene

4.3 Functional Groups

Alcohols

General Formula: -C-OH, or R-OH

Naming: The compound's name will end in -ol.

Worked Example:

Note:

- Using **–ol** as a suffix will not occur when a functional group of higher priority is attached to the carbon chain.
- In this case the presence of the –OH functional group is indicated using the prefix –**hydroxy-**

For Example:

Primary, Secondary and Tertiary Alcohols

Alcohols can also be identified as according to how many carbon atoms are bonded to the carbon atom attached to the hydroxyl group.

- **Primary Alcohols** – OH is attached to a carbon which is attached to **one** other carbon atom.

- **Secondary Alcohols** – OH is attached to a carbon which is attached to **two** other carbon atoms.

- **Tertiary alcohol** – OH is attached to a carbon which is attached to **three** other carbon atoms.

Reactions of alcohols

1. **oxidation of primary alcohols → aldehyde → carboxylic acid**

Task: Write the half equations and full equations for the oxidation of propan-1-ol by acidified potassium permanganate to form propanal.

2. **oxidation of secondary alcohols → ketone**

Task: Write the half equations and net equations for the oxidation of propan-2-ol by acidified potassium dichromate.

3. **Tertiary alcohols are not oxidised**

4. **Alcohols + carboxylic acids → esters + water**

Properties of alcohols

- Due to the presence of the –OH group, alcohols exhibit hydrogen bonding.
- This means that alcohols will tend to have higher melting and boiling points than other hydrocarbons of similar molar mass.
- The hydrogen bonding also means alcohols have a relatively high solubility in water – although the solubility decreases as the length of the hydrocarbon chain increases.

- Due to the openness of the hydrocarbon chain primary alcohols tend to have a higher boiling point than tertiary alcohols (this only applies to alcohols of similar molar mass).

Aldehydes

General formula:

Naming: Aldehydes are named using the suffix **–al** in the place of the 'e' on the end of the hydrocarbon's name.

For example:

- Aldehydes (and ketones) contain the –C=O functional group which is called the carbonyl group.
- The presence of this carbonyl group causes aldehydes to exhibit dipole-dipole interactions.
- This gives aldehydes higher melting points, boiling points and solubilities in water than other hydrocarbons of similar size (however these are not as pronounced or magnified as in alcohols which exhibit hydrogen bonding).

Ketones

General formula:

Naming: Ketones are named using the suffix **–one** in the place of the 'e' on the end of hydrocarbon's name.

For example:

- The properties of ketones are very similar to those of aldehydes.
- Ketones are not oxidised to form carboxylic acids.
- Ketones are formed by the oxidation of secondary alcohols.

General formula:

Naming: carboxylic acids are named using the suffix –**oic acid** in place of the 'e' on the end of the hydrocarbon's name.

For example:

- Because of the presence of the –C=O and –OH groups carboxylic acids have high solubilities in water, melting points and boiling points when compared to other organic compounds of similar molar mass.
- As with alcohols, aldehydes and ketones; the solubility of carboxylic acids decrease as the length of the carbon chain increases.

- Carboxylic acids are weak acids as they do not completely ionise when dissolved in water.

- Carboxylic acids are formed by the oxidation of primary alcohols and aldehydes.

Esters

General formula:

Naming: esters are made by reacting a carboxylic acid with an alcohol. Their name is derived from the two reacting components; where the **yl** comes from the alcohol reactant and the **oate** comes from the acid reactant.

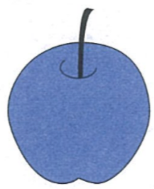
e.g. 1 ethan**ol** + methan**oic acid** → ethy**l** methan**oate** + water

Esterification is the name for the chemical reaction in which esters are made.

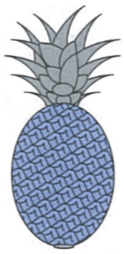
Example:
Write the equation for the reaction between butan-1-ol and propanoic acid.

Properties of Esters

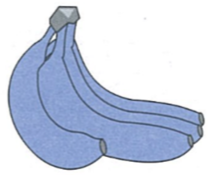
- Esters have similar boiling points to aldehydes and ketones with the same number of C atoms because of dipole-dipole forces of attractions and dispersion forces.
- Small esters are soluble in water but the solubility decreases as the length of the carbon chain increases.
- Many esters have their own distinctive fruity smell.



methyl butanoate



ethyl butanoate



pentyl ethanoate

Amides

General formula:

Naming: amides are named using the suffix –**amide** in place of the 'e' on the end of the hydrocarbon's name.

For example:

- Amides can be produced by reacting ammonia with carboxylic acid.
- The product is then heated to remove the water.

Properties of Amides

- The presence of the NH_2 and C=O groups means that amides form strong hydrogen bonds and consequently have high melting points for their size and are soluble in water.
- Solubility decreases as the size of the molecules increases.
- Although the presence of the $-NH_2$ would suggest otherwise, amides tend to form neutral solutions.

4.3 Summary Questions

Question 1.
Name the following compounds

Question 2
Name the following organic compounds

Question 3.
Draw the structural formula for each of the following.

(a). 2-iodopropan-2-ol

(b). 4,5-difluoro-6-methyloctan-2-ol

Question 4.

(a). Use half equations to write the balanced equations for acidified $K_2Cr_2O_7$ oxidising butan-1-ol.

(b). Use half equations to write the balanced equations for the reaction between acidified $KMnO_4$ and pentan-3-ol.

(c). Write the equation for the complete oxidation of butan-1-ol by oxygen gas.

Question 5.

Name the following

Question 6.
Draw the structural formula for each of the following:
(a). 3,4-dichloropentanal

(b). 3-methyloctan-4-one

(c). hexanoic acid

(d). 3,3,3-triiodopropanal

Question 7.
Name the ester formed in each of the following, and draw its structural formula.

(a). methanol + propanoic acid →

(b). hexanoic acid + propan-1-ol →

(c). heptan-1-ol + ethanoic aicd →

Question 8
What organic reactants could be used to produce the following esters?
(a). ethyl propanoate

(b). octyl butanoate

(c). propyl methanoate

Question 9
Name the following compounds.

Question 10
Draw the structural formula of the following
(a) 4,5,6-triiodoheptanamide

(b) 3-chloro-4-methypentanamide

4.4 Amines and α-Amino Acids

Amines

General formula:

Naming: The compound's name will end in -amine

For Example

When a functional group of higher priority is attached to the carbon chain, the –NH_2 functional group is indicated using the prefix **-amino-**

α-Amino Acids

- These compounds are the building blocks of proteins.
- They have an amine and a carboxyl group attached to the same carbon.
- This carbon is called the alpha (α) carbon.

Zwitterion Formation:

- Under some circumstances the amine group on the **α**-amino acid removes a proton (H^+) from the carboxylic group on the **α**-amino acid.
- The **α**-amino acid becomes a neutral ion that has a positive region (NH_3^+) and a negative region (COO^-).
- This neutral ion that possesses both a positive and negative charge is called a **zwitterion.**

For example:

Properties of α-amino acid and Proteins

- The properties of the carbon chain (R group) attached to the **α**-carbon that determine the properties of the **α**-amino acid.

Case 1 – If R is a hydrocarbon, it will be neutral and non-polar.

Case 2 – R has an amine group at the end, it will be basic and polar

Case 3 – R has a carboxylic acid group at the end, it will be acidic and polar.

4.4 Summary Questions

Question 1.
Name the following compounds:

Question 2
Glycine is the simplest amino acid. Comment on its polarity and acidity.

Question 3
Write the equation for glycine dissolving in:

(a) Water

(b) NaOH solution

(c) HCl solution

4.5 Reactions of Hydrocarbons

Addition Reactions

- Addition reactions occur when **alkenes** and **alkynes** have their double bonds broken and elements such as halogens are added into the carbon chain.

Substitution Reactions

- Substitution reactions occur when alkanes and aromatic compounds reach so that the hydrogen atom is removed and another element such as a halogen is substituted into its position on the hydrocarbon chain.

- For example:

- Alkanes and aromatic compounds are relatively inert.
- Substitution reactions need moderately high temperatures (250 °C) and/or UV light.
- Are usually slower than additional reactions

Combustion Reactions

- All hydrocarbon compounds can be burnt in oxygen.
- If complete combustion occurs, then the only products are carbon dioxide and water vapour.
- The production of energy by burning fossil fuels is the major form of energy production on Earth.

4.5 Summary Questions

Question 1

Write the equation for the following reactions. Show the structural formula for all organic compounds.

a. Ethene + Cl_2

b. Hexane + Br_2

c. but-1-ene + HBr

d. C_7H_{16} + O_2

4.6 Polymerisation

- A monomer is a small molecule that can be joined many times to form a polymer.
- **Polymerisation** is the chemical process by which many monomers are linked to each other to form large chain molecules called polymers.

Two types of polymerisations are:

i **Addition Polymerisation**

- The monomer is an alkene
- The polymer is formed by the breaking of the double bond in the simple alkene and then linking the pieces together.

ii **Condensation Polymerisation**

- One monomer is a di-carboxylic acid and the other is either a di-alcohol or a di-amine.
- If the monomer is a di-alcohol the polymer formed will be a polyester.
- If the monomer is a di-amine then the polymer is a polyamide.
- In both cases, the other product will be water, hence the name condensation polymer.

Polypeptides and proteins

- Polypeptides are chains of α-amino acid.
- Proteins are made up of one or more polypeptide molecule.

- Proteins are naturally occurring condensation polymers that have α-amino acids joined together in a vast arrangement of different sequences.
- The mechanism by which the α-amino acid polymerise is:
  - A hydrogen atom is removed from the amine group from one α-amino acid molecule and an OH group is removed from the carboxyl end of another α-amino acid molecule.

  - The two molecules then join at the sites where the H and OH are missing in what is called a peptide bond.

  - The also occurs at the other ends of the α-amino acid molecule. When many α-amino acid molecules join together, the polymer is called a polypeptide.

  - One polypeptide molecule can join or bond to another polypeptide molecule because of interactions (dispersion forces, dipole-dipole interactions or hydrogen bonds) between the side chains section.

  - The amide linkage, or peptide bond, is the key structure to identity when describing proteins.

- The sequence of the repeating amino acid monomers gives the protein its primary structure.
- The primary structure of a protein relates to structure by the covalently bonded atoms in the protein but not including any disulphide bridges.

- A protein may contain between 50 and 2000 repetitions of the amino acid monomers.

- The R side chain represents the remaining carbon region of any of the 20 amino acids that make up proteins.
- It is common practice to use a 3-letter or a 1-letter abbreviation of the amino acid rather than R when drawing proteins.
- The polarity of the side chain chain tends to affect the interactions of that region of the molecule with water.
- Generally the non-polar side chain region of the protein tend to be the core of the protein whereas the polar or charged regions tend to be at the surface.

Primary bonding within the atoms in a protein chain and secondary bonding is between charged regions within protein chain can affect the shape and properties of the protein molecule.

If the hydrogen bonding between amide and carbonyl groups is within a single chain, it tends to pull the protein chain into a coiled helix structure (α-helix).

If the hydrogen bonding between amide and carbonyl groups is in adjacent chains, it tends to cause folds or pleats in the protein chains (ß-plated sheets)

Bonding between R region or side chains that contribute to the overall 3D structure of the protein. The bonding between the side chains may be hydrogen bonding, dipole-dipole interactions, dispersion forces, ionic interactions or disulfide bridges.

4.6 Summary Questions

Question 1

Show what polymers can be formed from the following monomers

4.7 Organic Solvents

The solubility of one substance in another can be difficult to predict and is dependent on factors such as the nature of intermolecular forces within the solvent and solute, intermolecular forces between solvent and solute molecules, quantities of solvent and solute, temperature….

But generally:

- Polar solutes dissolve in polar solvents
- Non-polar solutes dissolve in non-polar solutes

Polar Solvents include:

- Alcohols (-OH)
- Amines ($-NH_2$)
- Aldehydes (-CHO)
- Ketones (-C=O)
- Carboxylic acids (-COOH)

Non-polar Solvents include:

- Alkanes
- Alkenes
- Alkynes
- Esters

As the length of the hydrocarbon chain increases, the molecules listed in polar solvents tend to become less polar and more non-polar in nature.

4.7 Summary Questions

Question 1

Explain how a small amount of motor oil could be removed from a concrete driveway?

Question 2

Methylated spirits is useful for cleaning windows. Explain what sort of materials methylated spirits would have trouble removing and explain why it doesn't leave streaks on windows.

Question 3

Functional group	General Formula	Name begins/end in	Solubility in water	Produced by
-Cl -I -Br (haloalkane)				Substitution Addition
C=C Alkene				NA
$-NH_2$ (primary				NA

amine)				
-OH (alcohols)				Hydration of an
-CHO (aldehydes)				Oxidation of a
Ketones				Oxidation of a
-COOH (carboxylic acids)				Oxidation of a or of an
(esters)				Alcohol with

Question 2

Reactants	Organic Products	Observations
Primary alcohol + $KMnO_4$ (acidified)		
Secondary alcohol + $K_2Cr_2O_7$ (acidified)		
Tertiary alcohol + $KMnO_4$ (acidified)		
Alkane + Cl_2 (with UV light)		
Alkyne + Cl_2		

Question 3

Combustion

$$\begin{bmatrix} \text{Hydrocarbons} \\ \text{Alcohols} \\ \text{Aldehydes, Ketones} \\ \text{Ester} \\ \text{Carboxyloc acids} \end{bmatrix} + O_2 \rightarrow$$

Substitution and Addition

Alkane + Halogen $\rightarrow$

Alkene + Halogen $\rightarrow$

Reactions of Esters:

4.8 Empirical Formula Calculations

Empirical Formula: Provides the simples whole number ratio of moles of each element present.

Molecular Formula: Shows the actual whole number ratio of moles of each element present.

Structural Formula: Indicates how the atoms if each elements are bonded to each other.

For example:

Ethanoic Acid:

- Empirical formula CH_2O
- Molecular formula $C_2H_4O_2$
- Structural formula is:

Empirical formula problems may be either:

- Simple i.e. the masses of the elements in the compounds (or %) are given.
- Complex (one sample) – a single sample is burnt or reacted.
- Complex (multi-sample) –two or more different sized samples are reacted.

Worked Example – 'simple type'

A 12.00g sample of substance contains 6.56 g of carbon, 1.10 g of hydrogen while the remainder is oxygen.
(a). Find its empirical formula
(b). If its molecular mass is 88.1, find its molecular formula.

Empirical Formula – 'complex type'

An organic compound was known to contain only carbon, hydrogen and oxygen. A 6.36g sample was burnt and the products formed collected (3.01g of water and 7.36g of carbon dioxide).

(a) Determine the empirical formula.

(b) Find the molecular formula of the molecular mass is 228g

Empirical Formula – 'complex type' two samples, same mass.

A 0.6578g sample of a compound which was known to contain only C, H, O, and S was completely burnt in excess oxygen. This produced 0.7413g of carbon dioxide and 0.4551g of water. The sulfur present was oxidised to the sulfate and precipitated as barium sulfate – 1.966g being recovered.

(a). Determine the empirical formula.

(b). A sample of the compound was vaporised and found to have a density of 3.49 g L^{-1} at S.T.P. Determine the molecular formula.

Empirical Formula – complex type – two samples of different mass

A compound containing carbon, hydrogen, nitrogen and oxygen was analysed as follows. First a 1.476g sample was burnt and 2.320g of CO_2 and 0.3168g of H_2O were formed. A second sample (1.167g) was treated to convert all the nitrogen into ammonia. The ammonia was titrated and found to be 0.01389 mol.

(a) Calculate the empirical formula of the compound.

(b) A third sample of the compound (2.520g) was vapourised and occupied 336 mL at STP. Use this information to determine its molecular formula.