Organic Chemistry

Ms. Peace
Lesson 1

Homologous Series
Lesson 1: Homologous Series

- Objectives:
  - Reflect on previous knowledge of organic chemistry
  - Understand the term ‘homologous series’
  - Conduct the fractional distillation of crude oil
  - Understand and use the variety of different types of formula used in organic chemistry
Organic Chemistry

- Organic chemistry is the chemistry of carbon containing compounds.
- From the very simple: methane
- To the very complex: Haem B
Types of Formula

- **Empirical Formula**: $C_4H_8O$  
- **Molecular Formula**: $C_4H_8O$  

- **Full Structural Formula**
  - Displayed formula

- **Condensed Structural Formula**
  - Note the '=' used for the C=C double bond

- **Skeletal formula**
  - Not required but v. useful
# Carbon Chains

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular Formula</th>
<th>Projection Formula</th>
<th>Condensed Structural Formula</th>
<th>Boiling Point (in °C)</th>
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<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>H—C—C—H</td>
<td>CH₄</td>
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<td>Ethane</td>
<td>C₂H₆</td>
<td>H—C—C—H</td>
<td>CH₃CH₃</td>
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<td>Propane</td>
<td>C₃H₈</td>
<td>H—C—C—C—H</td>
<td>CH₃CH₂CH₃</td>
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<tr>
<td>n-Butane*</td>
<td>C₄H₁₀</td>
<td>H—C—C—C—C—H</td>
<td>CH₃CH₂CH₂CH₃ or CH₃(CH₂)₃CH₃</td>
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<tr>
<td>n-Pentane*</td>
<td>C₅H₁₂</td>
<td>H—C—C—C—C—C—H</td>
<td>CH₃CH₂CH₂CH₃CH₃ or CH₃(CH₂)₃CH₃</td>
<td>36</td>
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<tr>
<td>n-Hexane*</td>
<td>C₆H₁₄</td>
<td>H—C—C—C—C—C—C—H</td>
<td>CH₃CH₂CH₂CH₃CH₂CH₃ or CH₃(CH₂)₄CH₃</td>
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<td>n-Heptane*</td>
<td>C₇H₁₈</td>
<td>H—C—C—C—C—C—C—C—H</td>
<td>CH₃(CH₂)₃CH₃</td>
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<td>n-Octane*</td>
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<tr>
<td>n-Nonane*</td>
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<td>n-Decane*</td>
<td>C₁₀H₂₂</td>
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<td>CH₃(CH₂)₆CH₃</td>
<td>174</td>
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</tbody>
</table>
Empirical Formulas

- Empirical formula: simplest whole number ratio of the atoms it contains.
- Molecular: actual number of atoms present
- **Example**: What is the empirical formula of ethane, $\text{C}_2\text{H}_6$?

$\text{CH}_3$
Homologous Series

- A homologous series is a family of compounds that differs only by the length of its hydrocarbon chain.

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

- Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds.
Structural Formulas

- Full structural formula – graphic formula showing every bond and atom. Usually 90° and 180° angles are used to show the bonds because this is the clearest representation on a 2-dimensional page, although it is not the true geometry of the molecule. *(MUST DRAW H’s!)*
Condensed Structural Formulas

- Condensed structural formula – often omits bonds where they can be assumed, and groups atoms together. It contains the minimum information needed to describe the molecule unambiguously.
Homologous Series and Boiling Points

- What do you think will be the trend in melting/boiling points as you go down a homologous series?

- Why?
Functional Groups

- Functional groups are the reactive parts of molecules

- Identification of different classes: alkanes, alkenes, alkynes, halogenoalkanes, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, amines, amides, nitriles and arenes

- Identification of typical functional groups in molecules eg phenyl, hydroxyl, carbonyl, carboxyl, carboxamide, aldehyde, ester, ether, amine, nitrile, alkyl, alkenyl and alkyny
<table>
<thead>
<tr>
<th>Class</th>
<th>General Formula</th>
<th>Example</th>
<th>Common Name (Systematic Name)</th>
<th>Common Suffix/Prefix (Systematic)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrocarbons</strong></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Alkanes</td>
<td>RH</td>
<td>CH₃CH₃</td>
<td>ethane</td>
<td>-ane</td>
</tr>
<tr>
<td>Alkenes</td>
<td>RR’C=CR”R’&quot;</td>
<td>H₂C=CH₂</td>
<td>ethylene (ethene)</td>
<td>-ene</td>
</tr>
<tr>
<td>Alkynes</td>
<td>RC≡CR’</td>
<td>H≡C≡CH</td>
<td>acetylene (ethyne)</td>
<td>(-yne)</td>
</tr>
<tr>
<td>Arenes</td>
<td>ArH&quot;</td>
<td></td>
<td>benzene</td>
<td>-ene</td>
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<tr>
<td><strong>Halogen-Containing Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Alkyl halides</td>
<td>RX</td>
<td>CH₃CH₂Cl</td>
<td>ethyl chloride (chloroethane)</td>
<td>halide (halo-)</td>
</tr>
<tr>
<td>Aryl halides</td>
<td>ArX&quot;</td>
<td></td>
<td>chlorobenzene</td>
<td>halo-</td>
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<tr>
<td><strong>Oxygen-Containing Compounds</strong></td>
<td></td>
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<tr>
<td>Alcohols</td>
<td>ROH&quot;</td>
<td>CH₃CH₂OH</td>
<td>ethyl alcohol (ethanol)</td>
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<tr>
<td>Phenols</td>
<td>ArOH&quot;</td>
<td></td>
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<td>-ol</td>
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<td>Ethers</td>
<td>ROR’</td>
<td>H₂CH₂COCH₂CH₃</td>
<td>diethyl ether</td>
<td>ether</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>RCHO</td>
<td></td>
<td>acetaldehyde (ethanal)</td>
<td>-aldehyde (-al)</td>
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<td>Ketones</td>
<td>RR’C=O</td>
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<td>Carboxylic acids</td>
<td>RCO₂H</td>
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<td>acetic acid (ethanoic acid)</td>
<td>-ic acid (-oic acid)</td>
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<td><strong>Carboxylic Acid Derivatives</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esters</td>
<td>RCO₂R’</td>
<td></td>
<td>methyl acetate (methyl ethanoate)</td>
<td>-ate (-oate)</td>
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<tr>
<td>Amides</td>
<td>RCONHR’</td>
<td>CH₃CNHCH₃</td>
<td>N-methylacetamide</td>
<td>-amide</td>
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<td><strong>Nitrogen-Containing Compounds</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amines</td>
<td>RNH₂, RNHR’&quot;, RNR’”</td>
<td>CH₃CH₂NH₃</td>
<td>ethylamine</td>
<td>-amine</td>
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<tr>
<td>Nitriles</td>
<td>RC≡N</td>
<td>H₂C≡N</td>
<td>acetonitrile</td>
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<tr>
<td>Nitro compounds</td>
<td>ArNO₂&quot;</td>
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<td>nitrobenzene</td>
<td>nitro-</td>
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</tbody>
</table>

*“R indicates an alkyl group” "Ar indicates an aryl group."
Saturated vs Unsaturated

- Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds
- Benzene is an aromatic, unsaturated hydrocarbon
Key Points

- Organic chemistry is the chemistry of carbon containing compounds

- The melting and boiling point increases as you increase carbons in a homologous series

- Benzene is an aromatic, unsaturated hydrocarbon
International Mindedness

- A small proportion of nations have control over the world’s oil resources. The interdependence of the countries that are net importers and those that are net exporters is an important factor in shaping global policies and economic developments.

- The octane rating (octane number) can be described as a standard measure of the performance of the fuel used in cars and aircraft. Octane ratings often vary quite widely regionally throughout the globe, and are complicated by the fact that different countries use different means of expressing the values.
Utilization

- Fractional distillation makes great use of many petrochemicals.

- Dyes, pesticides, herbicides, explosives, soap, cosmetics, synthetic scents and flavourings.
Lesson 2

Isomers
Lesson 2: Isomers

Objectives:

- Describe the term structural isomer
- Draw a name the non-cyclic alkanes
- Draw and name the straight-chain alkenes
Isomers

- Compounds with the same molecular formula but different structural formula

- The 20 different C₄H₈O compounds are isomers of each other

- These are all structural isomers
  - Same number of each atom, but bonded in a different order

- You would have even more if you included geometric and optical isomers
Formulas

- Draw the compound with the formula $\text{C}_4\text{H}_8\text{O}$
What did you get?

- Clearly a molecular formula is not enough!
Structural Isomers of the Alkanes

- The (non-cyclic) alkanes, alkynes, ketones, alcohols, aldehydes, and carboxylic acids have the general formula $\text{C}_n \text{H}_{2n+2}$.
IUPAC Nomenclature

Naming Branched Alkanes (IUPAC)

1. Root name: name of longest continuous C chain (parent chain)
   - 2 equally long? Choose the one with more branches
2. Number C atoms in chain, starting at end with first branch
3. Identify substituents, give each a number (C it is connected to)
   - Two or more identical substituents: use prefixes (di-, tri-, tetra-, etc.)
4. List substituents alphabetically before root name
   - Do not alphabetize prefixes
5. Punctuation: commas separate numbers from each other
   - hyphens separate numbers from names
   - no space between last substituent & root name
<table>
<thead>
<tr>
<th>CLASS OF ORGANIC COMPOUND</th>
<th>STRUCTURE OF THE FUNCTIONAL GROUP</th>
<th>IUPAC GROUP PREFIX</th>
<th>IUPAC GROUP SUFFIX</th>
<th>EXAMPLES</th>
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<td>[ ]</td>
<td>-</td>
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<td>Halides</td>
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<td>(X = F, Cl, Br, I)</td>
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<td>(X = F, Cl, Br, I)</td>
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<td>1-nitrobutane</td>
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<td>Class</td>
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<td>Prefix/Suffix</td>
<td>General Structure</td>
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<td>-nitrile</td>
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<tr>
<td>arenes</td>
<td>phenyl</td>
<td>-yl benzene</td>
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</tbody>
</table>
Boiling Points

- The boiling point decreases as the intermolecular forces decrease, and branching of the hydrocarbon increases.

- The boiling point of alcohols is higher than that of alkanes due to the O-H group.

- Alcohols have a lower volatility than that of alkanes.
Primary, Secondary, Tertiary

The name depends on the number of carbons directly attached to the red carbon (not hydrogens!)

- **Methane (unique)**
  - 0 carbons attached

- **Primary (1°) carbon**
  - 1 carbon directly attached

- **Secondary (2°) carbon**
  - 2 carbons attached

- **Tertiary (3°) carbon**
  - 3 carbons attached

- **Quaternary (4°) carbon**
  - 4 carbons attached

Amines: count the number of carbons directly attached to the nitrogen

- **Ammonia (unique)**
  - 0 carbons

- **Primary (1°) amine**
  - 1 carbon directly attached

- **Secondary (2°) amine**
  - 2 carbons

- **Tertiary (3°) amine**
  - 3 carbons

- **Quaternary (4°) amine (ammonium)**
  - 4 carbons

You should be able to identify for haloalkanes, alcohols, and amines
Naming Straight-chain alkanes

- **Suffix:**
  - Tells us the functional group of the molecule
  - For alkanes it is ‘-ane’

- **Prefix:**
  - Tells us the length of the longest carbon chain:
    - 1 carbon: *meth-*
    - 2 carbons: *eth-*
    - 3 carbons: *prop-*
    - 4 carbons: *but-*
    - 5 carbons: *pent-*
    - 6 carbons: *hex-*

- **Example 1:** ethane
  - ![Ethane](image)

- **Example 2:** butane:
  - ![Butane](image)

- **Task:** write in the names of the 4 straight chain alkanes next to your diagrams from last slide
Naming branched-chain alkanes

- Start by naming the longest chain

- Add extras to say the size of a branch, its position and how many of that branch

  **Branch Size:**
  - 1 carbon: methyl-
  - 2 carbons: ethyl-
  - 3 carbons: propyl-

  **Position:**
  - Number the carbons in the longest chain
  - Choose numbers to minimise the total numbers used

  **Number of same branches**
  - One branch – nothing
  - Two branches – di-
  - Three branches – tri-
  - Four branches – tetra-

- **Example 1:** 2-methylpropane

- **Example 2:** 2,3-dimethylbutane

- **Task:** Name the remaining alkanes
Key Points

- Structural isomers have the same number of each atom but they are connected differently.

- When naming compounds:
  - The longest carbon chain forms the prefix.
  - The functional group tells you the suffix.
    - Sometimes numbers need to be used to tell you where this functional group is.
  - Side chains and other groups are named according to what they are, how many there are and their position.
Lesson 4: Alkanes

- Objectives:
  - Explain the stability of the alkanes
  - Observe the combustion of alkanes
  - Describe the free-radical substitution reactions of alkanes and its mechanism
  - Observe the free-radical substitution of hexane
Combustion of Alkanes

- The alkanes really don’t do much
  - Combustion is one of two notable reactions (this is why we use them for fuels)

- Complete combustion:
  - alkane + oxygen → carbon dioxide + water

- Incomplete combustion:
  - Alkane + oxygen → carbon + carbon monoxide + carbon dioxide + water
  - The amounts of C, CO and CO₂ will vary depending on conditions
Why Good Fuels?

- To do:
  - Use Table 12 in the data booklet to help you determine the trend in energy released per gram by combustion of the alkanes.
  - Use bond enthalpies to help you explain the trend noted above.
  - What do you think should be the characteristics of a good fuel?
  - Use the above to decide and explain which out of methane and octane is a better fuel.
Unreactivity of Alkanes

- There are at least two reasons why alkanes are so unreactive:
  - High strength of C-C and C-H bonds that is generally unfavorable to break
  - C-C and C-H bonds are essentially non-polar and are unlikely to attract polar molecules or ions
Halogenation

- Alkanes will undergo halogenation if reacted with a halide in the presence of u.v. light.

- For example:
  - \( C_2H_6(g) + Cl_2(g) \xrightarrow{\text{u.v.}} CH_3CH_2Cl(g) + HCl(g) \)
  - ethane \rightarrow chloroethane

- This reaction is an example of free radical substitution
Halogenation

- An atom or group is replaced by a different group or atom
- The replacement of one hydrogen atom in the molecule by one halogen atom
- The reaction can be difficult to control and a number of products, some involving multiple steps, can be formed

\[
\text{ethane} \quad \text{Cl} = \text{Cl} \quad \text{Heat or light} \quad \text{chloroethane}
\]
Radical

- Radicals are species with unpaired electrons
  - They are crazy reactive

- Halogens form radicals when hit by uv light of the right frequency:
  - \( \text{Cl}_2 \text{ u.v} 2 \text{ Cl}\cdot \)
  - The dot after the Cl represents the unpaired electron and tells us we have a radical
  - This process is called homolytic fission – the bond breaks equally with one electron going to each chlorine
Reaction Mechanism: Free Radical Substitution

▶ **Initiation**

- Radicals formed by homolytic fission

▶ **Propagation**

- These steps feed each other the radicals needed to continue

▶ **Termination**

- Any two radicals can combine to terminate the reaction
- Concentration of radicals is low so this is a rare event

- A single radical can cause thousands of cycles of the propagation stage before it reaches termination
- This same mechanism applies to all of the halogens
- The alkane can be substituted multiple times, until every H has been replaced
Free Radical Substitution

https://www.youtube.com/watch?v=XAWWf86TJOc
Extension:

- Research the role of free radical reactions in the depletion of the ozone layer
Key Points

- Alkanes are pretty unreactive

- They release a lot of energy on combustion, and are easy to handle which makes them good fuels

- Undergo free radical substitution to form halogenoalkanes and a hydrogen halide in the presence of UV light
Lesson 5: Alkenes

- Objectives:
  - Describe the main addition reactions of the alkenes
  - Extract an alkene from a citrus fruit
Reactivity of Alkenes

- Alkenes are considerably more reactive than alkanes and are a major industrial feedstock.

- The reactivity is due to the double bond:
  - The double bond contains 4 electrons.
  - This is a significant amount of charge which:
    - Makes it attractive to electrophiles.
    - Enables it to polarise approaching molecules.

- Most reactions of alkenes are addition reactions where two molecules come together to make one new one.
Alkenes and hydrogen

- Alkene + hydrogen → alkane

\[
\begin{align*}
\text{H}_3\text{C} &= \text{C} - \text{C} & & \text{Ni cat.} & & \text{H}_3\text{C} &= \text{C} - \text{C} \\
\text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H}
\end{align*}
\]

- Reaction conditions:
  - Hot
  - Ni catalyst

- This is an addition reaction, in which the hydrogen adds across the double bond
Alkenes and hydrogen halides

- Alkene + hydrogen halide $\rightarrow$ halogenoalkane

![Chemical structure](image)

- Reaction conditions:
  - This reaction occurs very readily and needs no special conditions

- This is an addition reaction, in which the hydrogen halide adds across the double bond

Main
Alkenes and halogens

- Alkene + halogen $\rightarrow$ dihalogenoalkane

- Reaction conditions:
  - This reaction occurs very readily and needs no special conditions
Alkenes and water

- Alkene + water $\rightarrow$ alcohol

Reaction conditions:
- Water must be steam
- Phosphoric or sulphuric acid catalyst

This is the process used to make industrial ethanol
Polymerization

- Under the right conditions, alkene molecules will add to each other creating a polymer

\[ \text{C} = \text{C} \quad \text{C} = \text{C} \quad \text{C} = \text{C} \quad \rightarrow \quad \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \]

- Conditions vary from alkene to alkene but often include high pressure, temperature and a catalyst

- The carbons in the C=C double bonds form the carbon chain, everything else hangs off this chain

- The basis of the plastics industry!
Homework

- Research the economic importance of alkenes including:
  - Manufacture of margarine
  - Manufacture of ethanol
  - Polymerisation

- Page 455-457 in textbook
Key Points

- Alkenes undergo addition reactions with:
  - Hydrogen
  - Hydrogen halides
  - Halogens
  - Water (steam)

- Alkenes undergo addition polymerisation

- Alkenes are very economically important due to the range of products they can make
We Are Here
Lesson 6: Alcohols

- Objectives:
  - Explain the relative ease of combustion of the alcohols
  - Describe the oxidation reactions of the alcohols
  - Investigate the oxidation reactions of the alcohols
Alcohols as Fuels

- Alcohols combust more readily than equivalent alkanes but release less energy since they are already partially oxidised.

**Alcohol + oxygen → carbon dioxide + water**

- Alcohols are used as fuels:
  - As a fuel for cars – either pure or blended with petrol
  - Methanol as fuel for competitive motorsports including dragsters and monster trucks
Oxidation of alcohols

The most important reactions of the alcohols are their oxidations.

A range of compounds will oxidize them so the oxidizer is often represented as [O].

One oxidising agent you need to know is potassium dichromate, $K_2Cr_2O_7$.

When using this, orange Cr (VI) is reduced to green Cr (III).
Utilization

- Breathalyzer test: blow into bag through tube of acidified $K_2Cr_2O_7$ crystals. If orange crystals turn green, this indicates presence of a lot of ethanol (high BAC).
Oxidation reaction scheme

Primary alcohol:

Primary alcohol $+ \quad [O]$ (add $[O]$ to $R-OH$) $\rightarrow$ Aldehyde

Distil as formed

Aldehyde $+ \quad [O]$ (heat under reflux) $\rightarrow$ Carboxylic acid

Secondary alcohol:

Secondary alcohol $+ \quad [O]$ $\rightarrow$ Ketone

No reaction

Tertiary alcohol:

Tertiary alcohol $+ \quad [O]$ $\rightarrow$ No reaction
Oxidation of Primary Alcohol

- To stop rxn at aldehyde stage, distill aldehyde from the rxn mixture as soon as it is formed.

- If complete oxidation to carboxylic acid is desired, heat the mixture under reflux so that none of the carboxylic acid can escape.
Oxidation

Distillation

Reflux

Water Out

Water In

Reactants

Heat

Water
Esterification

Alcohol + carboxylic acid $\rightarrow$ ester + water

Ethanol + ethanoic acid $\rightarrow$ ethyl ethanoate + water

Esters, varied uses—perfumes, food flavourings, solvents, nitroglycerin, biofuels and painkillers
This reaction is described as a nucleophilic substitution
- The alcohol acts as a nucleophile—substitutes (replaces) the OH group of the carboxylic acid
- The esterification reaction can be classified as a condensation reaction—two molecules join together
Key Points

- Alcohols are highly combustible

- Primary alcohols oxidize to form aldehydes, which oxidize to form carboxylic acids

- Secondary alcohols oxidize to form ketones

- Tertiary do not oxidize due to the 3 strong C-C bonds surrounding the –OH carbon
The label “organic chemistry” originates from a misconception that a vital force was needed to explain the chemistry of life. Can you think of examples where vocabulary has developed from similar misunderstandings? Can and should language ever be controlled to eliminate such problems?
Lesson 7

Halogenoalkanes
We Are Here

- Halogenoalkanes
- Reaction Pathways
- Nucleophilic Substitution
- Elimination
- Condensation
- Stereoisomerism
- Formulas
- Isomerism
- Functional Groups and Naming
- Alkanes
- Alkenes
- Alcohols
Objectives:

- Describe the substitution reactions of halogenoalkanes with a strong base
- Understand the $S_N^1$ and $S_N^2$ mechanisms for nucleophilic substitution
- Produce an animation showing the two different mechanisms
Nucleophilic Substitution

- One of the most important reactions undergone by halogenoalkanes is nucleophilic substitution.

- A nucleophile is a ‘nucleus-loving’ species that is attracted to positive charges.
  - Nucleophiles have either full negative charges or delta-negative charges.
  - Water and hydroxide are both nucleophiles.
    - In this case we can also call the reaction ‘hydrolysis’.

- The carbon in the carbon-halogen bond has a $\delta^+$ charge due to the greater electronegativity of the halogen.
  - This makes it susceptible to attack by nucleophiles.
Halogenoalkanes and strong bases

- A substitution reaction takes place, where the halogen atom is displaced by the hydroxide ion

$$\text{halogenoalkane} + \text{sodium hydroxide} \rightarrow \text{alcohol} + \text{sodium chloride}$$

- **Conditions:**
  - Aqueous base
  - Gently warmed (can occur at room temperature, but may be quite slow)

- This is a nucleophilic substitution. (Also called a condensation reaction)
  - The C attached to the halogen is $\delta^+$ due to the high electronegativity of the halogen
  - The $\text{OH}^-$ ion (our nucleophile) is attracted to the $\delta^+$ carbon
    - A nucleophile is a species with a negative charge or a lone pair that is attracted to positive/delta-positive atoms
$S_N 1$ – Unimolecular nucleophilic substitution

- **Unimolecular** because only one molecule is involved in the rate determining step

- The rate determining step involves the spontaneous breaking of the carbon-halogen bond and is a **heterolytic fission**, forming a halide ion and a carbocation intermediate
  - The stability of the carbocation intermediate is a key factor in $S_N 1$

**Note:** the curly arrows show the movement of pairs of electrons
$S_N1$ – Unimolecular nucleophilic substitution

- The attack by the nucleophile ($\text{OH}^-$) is very fast, but does need the carbocation to be formed first

- The rate is only dependent on the concentration of the halogenoalkane:
  - Rate = $k[\text{halogenoalkane}]$

- Leaving group strength: $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

- $S_N1$ reactions are best conducted using protic, polar solvents.
  - Have H joining to N or O and can participate in hydrogen bonding. Able to solvate both negative ions and positive ions in solution.
  - Ex: Water, ethanol, and ammonia
**S\textsubscript{N}2 – Bimolecular nucleophilic substitution**

- Bimolecular because two molecules are involved in the rate determining step

- In the rate determining step, the nucleophile (OH\textsuperscript{−}) attacks at the same time as the carbon-halogen bond breaks.
$S_N^2$ – Bimolecular nucleophilic substitution

- The reaction passes through a negative transition state where the carbon has a ‘half-bond’ to both the $-OH$ and the $-Br$ with an overall negative charge.

- The rate is dependent on both the concentration of the halogenoalkane and the nucleophile.
  - Rate = $k[\text{halogenoalkane}][\text{nucleophile}]$

- $S_N^2$ reactions are best conducted using aprotic, non-polar solvents.
  - Do not have H atom joined to N or O and cannot participate in hydrogen bonding. Good at solvating positive ions but not negative ions.
  - Ex: DMSO (dimethyl sulfoxide), propanone.
  - Act as proton donors.
$S_N^1$ or $S_N^2$?

- $1^\circ$ halogenoalkanes predominantly undergo $S_N^2$

- $2^\circ$ halogenoalkanes undergo a mix of $S_N^1$ and $S_N^2$

- $3^\circ$ halogenoalkanes predominantly undergo $S_N^1$
Things to Remember

- OH\(^-\) is a better nucleophile than H\(_2\)O due to the negative charge on the hydroxide making it more ready to attack positive ions
Understanding Check

- Write balanced equations, using condensed structural formulas, and name the products of the reactions of the following with dilute sodium hydroxide:
  - Bromoethane
  - 1-chloro-2-iodopropane
  - 3-chloro-3-ethylhexane

- Name and draw the mechanism for all 3.
Halogenoalkanes undergo substitution with strong bases to form alcohols

The reaction has two possible mechanisms:

- $S_N^1$: the C-X bond breaks and then the nucleophile attacks
- $S_N^2$: the nucleophile attacks at the same time as the C-X bond breaks

The mechanism depends on the halogenoalkane:

- $1^\circ$ - $S_N^2$
- $2^\circ$ - $S_N^1$ and $S_N^2$
- $3^\circ$ - $S_N^1$
Lesson 8

$S_N^1$ and $S_N^2$ Revisited
We Are Here

- Halogenoalkanes
- Reaction Pathways
- Nucleophilic Substitution
- Elimination
- Condensation
- Stereoisomerism
- Formulas
- Isomerism
- Functional Groups and Naming
- Alkanes
- Alkenes
- Alcohols
Lesson 10: $S_N^1$ and $S_N^2$ Revisited

- Objectives:
  - Understand why the nature of the halogenoalkane affects the mechanism of nucleophilic substitution reactions
  - Understand why $\text{OH}^-$ is a better nucleophile than $\text{H}_2\text{O}$
  - Understand the effect of the halogen on the rate of nucleophilic substitution reactions
  - Complete a short investigation into the factors affecting the rate of nucleophilic substitution
$S_N_1$ and $S_N_2$ Recap

 carbocation intermediate

transition state
S_N 1 and the carbocation

- The carbocation is an unstable species, and will often immediately attract the halide ion straight back.

- Alkyl groups surrounding the carbocation donate electron charge to it and stabilise it.

- In this diagram, the arrows on the bonds represent the charge donated by the surrounding alkyl groups.

- 3° carbocations have most surrounding alkyl groups and therefore are most stable, thus S_N 1 is preferred for 3° halogenoalkanes.
Mechanism and rate

- For $S_N^1$: $\text{rate} = k[\text{halogenoalkane}]$

- For $S_N^2$: $\text{rate} = k[\text{halogenoalkane}][\text{nucleophile}]$

- Since $S_N^1$ only depends on one reactant, it tends to be faster (all else being equal) than $S_N^2$

- Therefore, if we consider the rates of hydrolysis / substitution, as a rule of thumb:

  Tertiary > Secondary > Primary
SN₂ and steric hindrance

- Alkyl groups are physically bulky, and make it difficult for a nucleophile to attack the carbon: this is called steric hindrance.

- ¹卤代烷烃 only have one surrounding alkyl group so steric hindrance is low and SN₂ is favourable.

- ³卤代烷烃 have three surrounding alkyl groups so steric hindrance is high and SN₂ is unfavourable.

- The black arrows on the diagram are supposed to show possible avenues of approach by the nucleophile, red crosses show where they are blocked.
Changing the Nucleophile

- Water can act as our nucleophile:
  - Halogenoalkane + water $\rightarrow$ alcohol + hydrogen halide

- However, hydroxide is much better. Why?
  - Explain why using ideas from the bonding unit
Changing the Halogen

- The rate of substitution/hydrolysis varies greatly depending on the halogen atom.

- As a rule, with all else being equal, the rate changes as follows:

  Iodine > Bromine > Chlorine

- Explain why using ideas from the bonding unit.
Exploring Nucleophilic Substitution

- In this experiment you will explore the effect on the rate of nucleophilic substitution of:
  - The halogen atom involved
  - The position of the halogen atom
  - The nucleophile used

- The products of the reactions are colourless but since these reactions produce halide ions, we can use their precipitation reaction with silver ions to follow the reaction
Key Points

- The substitution mechanism followed depends on:
  - Stabilisation of the carbocation by surrounding alkyl groups
  - Steric hindrance of the carbocation by surrounding alkyl groups

- Hydroxide ions are better nucleophiles than water due to their strong negative charge

- Iodoalkanes react faster than chloroalkanes due to the C-I bond being weaker than the C-Cl bond
Lesson 9

Electrophilic Reactions and Benzene
Electrophilic Addition Reactions

- An electrophile is an electron-deficient species that can accept electron pairs from a nucleophile. Electrophiles are Lewis acids.

- Markovnikov’s rule can be applied to predict the major product in electrophilic addition reactions of unsymmetrical alkenes with hydrogen halides and interhalogens. The formation of the major product can be explained in terms of the relative stability of possible carbocations in the reaction mechanism.
Electrophilic Substitution Reactions

Benzene is the simplest aromatic hydrocarbon compound (or arene) and has a delocalized structure of bonds around its ring. Each carbon to carbon bond has a bond order of 1.5. Benzene is susceptible to attack by electrophiles.
Reduction Reactions

- Carboxylic acids can be reduced to primary alcohols (via the aldehyde). Ketones can be reduced to secondary alcohols. Typical reducing agents are lithium aluminium hydride (used to reduce carboxylic acids) and sodium borohydride.
The Story of Benzene

A new hydrocarbon isolated by Michael Faraday in 1825

Carbon = 92% Carbon (Atomic mass = 12)

Hydrogen = ? % (Atomic mass = 1)

Relative molecular mass = 78.

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>92</td>
<td>100-92 = 8</td>
</tr>
<tr>
<td>% divided by RAM</td>
<td>92 / 12 = 7.67</td>
<td>8 / 1 = 8</td>
</tr>
<tr>
<td>Divide by smallest</td>
<td>7.67 / 7.67 = 1</td>
<td>8 / 7.67 = 1.04</td>
</tr>
<tr>
<td>Ratio</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Benzene

**Molecular formula**

Known RAM / RMM of empirical formula

\[ 78 / (12 + 1) = 6 \]

The empirical formula is CH and the molecular formula is \( C_6H_6 \) suggesting that the molecule contained a large number of double bonds.
In 1865 after a dream about a snake biting its own tail, Kekulé suggested the following structure for benzene.
Lack of Reactivity

Chemists at the time were convinced that benzene (like other alkenes) should react with bromine in the dark at room temperature.

Observation: This did NOT happen with benzene.
Conclusion: Benzene more stable than a normal alkene
Thermodynamic Stability

Enthalpy of hydrogenation (addition of hydrogen) to cyclohexene was found to be $-119\text{kJmol}^{-1}$

\[
\text{Cyclohexene} + \text{H}_2 \rightarrow \text{Cyclohexane} \quad \Delta H = -119 \text{kJ mol}^{-1}
\]

\[
\text{Benzene} + 3\text{H}_2 \rightarrow \text{Cyclohexane} \quad \Delta H = \text{? kJ mol}^{-1}
\]
Since three double bonds are present in benzene, then the comparable reaction should liberate 3 times the energy of cyclohexene
\[ -(3 \times 119) = -357 \text{ kJ mol}^{-1} \]

Experimentally determined value for the hydrogenation of benzene \( \Delta H \) (hydrogenation) = -208kJ mol\(^{-1} \)

Benzene is more stable than predicted
Bond Lengths of Benzene

What benzene should look like

Bond lengths in single and double bonds should be different.

In benzene
1. All bonds are of equal length
2. The bond length is between a double bond and a single bond.
The bonds can’t be fixed

Resonance suggests the two structures rapidly alternate between the two forms.
The resonance explanation suggests that Benzene is in such rapid equilibrium between the two forms; we detect a ‘blurred’ combination of the two forms.

The electrons from the double bonds are therefore drawn as a circle shared equally between the carbon atoms.
Valence bond theory explains the bonding in benzene as a series of unhybridized $p$-orbitals which overlap forming a cloud of electron density above and below the molecule. The spreading of electrons STABILIZES the molecule.
Which drawing most accurately represents the structure and bonding in Benzene? Explain

Are any of the pictures completely incorrect? (i.e. not Benzene) if so which and why?

• **D is incorrect (cyclohexane not benzene!)**
• **A doesn’t show delocalized electrons**
• **Organic chemists tend to use B or C if they want to draw mechanisms**
Electrophilic Addition Reaction of Alkene

- Deduction of the mechanism of the electrophilic addition reactions of alkenes with halogens/interhalogens and hydrogen halides.
Electrophilic Addition Reaction of Alkene

First Stage

- The positive charge of the electrophile is attracted to the electron density of the double bond.
- As the electrophile approaches the double bond electrons in the H-X are repelled towards the X(halogen).
- The pi bond breaks, forming a carbocation—an ion with a positively charged carbon atom, while the H attaches and the halogen is left to form an ion.
- The initial breaking of the H-X is called heterolytic fission.
Electrophilic Addition Reaction of Alkene

Second Stage

- The halogen act as a nucleophile and attacks the carbocation
Asymmetric Alkenes

Addition to asymmetric alkenes

 propene + HBr

2-bromopropane

H \quad \text{CH}_3
\quad H \quad C \quad C \quad H
\quad H \quad Br

two possible products

1-bromopropane

H \quad \text{CH}_3
\quad H \quad C \quad C \quad H
\quad H \quad Br \quad H
Markovnikov’s Rule

- The formation of the major product can be explained in terms of the relative stability of possible carbocations in the reaction mechanism.

- When $H-X$ adds across the double bond of an alkene, the $H$ atom becomes attached to the $C$ atom that has the larger number of $H$ atoms already attached.
Stability of Carbocations

There are more electron releasing alkyl groups around the positively charged carbon.
Ethene with \( \text{Br}_2 \)

**Electrophilic addition of bromine to an alkene**

```
H
\( \text{C} \equiv \text{C} \) \( \delta^+ \) \( \text{Br} \) \( \delta^- \) \( \text{Br} \) \( \text{Br} \)
```

```
H
\( \text{C} \equiv \text{C} \) \( \text{H} \) \( \text{H} \) \( \text{H} \) \( \text{H} \)
```

STEP 1

```
H
\( \text{C} \equiv \text{C} \) \( \text{H} \) \( \text{H} \) \( \text{H} \) \( \text{H} \)
```

STEP 2

```
H
\( \text{C} \equiv \text{C} \) \( \text{H} \) \( \text{H} \) \( \text{H} \) \( \text{H} \)
```

Main
Nitration of Benzene

- **Step 1:** The formation of the electrophile-NO$_2^+$, which is formed when concentrated sulfuric acid reacts with concentrated nitric acid
  - a pair of electrons from the benzene $\pi$ delocalized system is used to form a bond to the NO$_2^+$ electrophile
- **Step 2:** The collision between the benzene molecule and the electrophile
  - Releases a pair of electrons to restore the $\pi$ delocalized system
Step 1: $\text{H-O-NO}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{H-O-NO}_2 + \text{HSO}_4^-$

Step 2: $\text{H-O-NO}_2 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{H}_3\text{O}^+ + \text{HSO}_4^-$

Step 3: $\text{Ph} + \text{NO}_2^+ \rightarrow \text{Ph-NO}_2^+$

$\text{Ph-NO}_2 + \text{HSO}_4^- \rightarrow \text{Ph-NO}_2 + \text{H}_2\text{SO}_4$
Nitration of Benzene

**Chemical Reaction:**

\[ \text{Benzene} + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4\text{ catalyst}} \text{nitrobenzene} \]

**Reaction Conditions:**

- Temperature: 50°C

**Mechanism:**

1. **Nucleophilic aromatic substitution:**
   - **Step 1:** Electron-rich aromatic ring attacks the nitrosonium ion (NO₂⁺).
   - **Step 2:** Nitration occurs, forming nitroarene and releasing a proton (H⁺).

This process is a fundamental reaction in organic chemistry, demonstrating the electrophilic substitution on an aromatic ring.
Reduction Reactions

Aldehyde

\[ \text{Reducing agent} \]

Primary alcohol

Ketone

\[ \text{Reducing agent} \]

Secondary alcohol
Reduction Reactions

\[
\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{1. LiAlH}_4} \xrightarrow{\text{2. } \text{H}_3\text{O}^+} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}
\]

propanoic acid \rightarrow propanol

\[
\text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{1. LiAlH}_4} \xrightarrow{\text{2. } \text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{CH}_2\text{OH}
\]

benzoic acid \rightarrow benzyl alcohol
Reducton Reactions

\[ \text{NO}_2 \xrightarrow{\text{Fe}_3/\text{HCl}_{30\%}} \text{NH}_3^+\text{Cl}^- \xrightarrow{\text{Na}_2\text{CO}_3} \text{NH}_2 \]
Reduction Reaction Equations

When writing the equations for reduction reactions

\[
\text{Reactant} + [\text{H}] \rightarrow \text{Product}
\]

The [H] represents the hydrogen from the reducing agent

Balance as needed
Lesson 10

Retrosynthesis
Synthetic Routes

- The synthesis of an organic compound stems from a readily available starting material via a series of discrete steps. Functional group interconversions are the basis of such synthetic routes.

- A retro-synthetic approach is often used in the design of synthetic routes.
  - Start with the target molecule and work backwards, using known reactions to get an appropriate and readily available starting material.

- Conversions with more than four stages will not be assessed in synthetic routes.
Lesson 11
Condensation Polymerisation
We Are Here

Organic Chemistry

- Halogenoalkanes
- Reaction Pathways
- Nucleophilic Substitution
- Elimination
- Condensation
- Stereoisomerism
- Formulas
- Isomerism
- Functional Groups and Naming
- Alkanes
- Alkenes
- Alcohols
Lesson 14: Condensation Reactions

- Objectives:
  - Describe with equations the condensation reactions of diacids with diols
  - Describe with equations the condensation reactions of diacids with diamides
  - Perform the nylon rope-trick
Polyesters

Polyesters form from monomers containing two functional groups

- For example dicarboxylic acids and dialcohols
- Each end of each molecule forms an ester linkage, allowing for long chains to build up

\[
\text{HO-C-\text{[\square]}-C-OH + HO-\text{[\square]}-OH} \\
\text{a dicarboxylic acid} \quad \text{a dialcohol} \\
\downarrow \\
\left[\text{C-\text{[\square]}-C-O-\text{[\square]}-O}\right]_n \\
\text{a polyester}
\]
Polyamides

- Similar to polyesters, polyamides form from monomers containing two functional groups
  - For example dicarboxylic acids and diamines
  - Each end of each molecule forms an amide linkage, allowing for long chains to build up

```
HO-C-__-C-OH + H2N-__-NH2
a dicarboxylic acid     a diamine

[C-__-C-NH-__-NH]_n
a polyamide
```
A quick note

- You can also get condensation polymerisation from monomers containing one of each of the functional groups.

- The best example is amino acids and proteins:
Key Points

- Polyesters form from monomers containing two acid and two alcohol groups

- Polyamides form from monomers containing two acid and two amine groups
Lesson 12

Geometrical Isomerism
We Are Here

Organic Chemistry

- Halogenoalkanes
- Reaction Pathways
- Nucleophilic Substitution
- Elimination
- Condensation
- Stereoisomerism
- Formulas
- Isomerism
- Functional Groups and Naming
- Alkanes
- Alkenes
- Alcohols

Main
Lesson 12: Geometrical Isomerism

Objectives:

- Understand the term stereoisomerism
- Understand and identify geometrical isomerism
- Understand the chemical significance of cis-trans isomerism
Isomers

- Stereoisomers are subdivided into two classes
  - Conformational isomers, which interconvert only by breaking and reforming a bond.
  - Configurational isomers are further subdivided into cis-trans and E/Z isomers and optical isomers.

- Cis-trans isomers can occur in alkenes or cycloalkanes (or heteroanalogues) and differ in the positions of atoms (or groups)
Stereoisomerism

- Stereoisomers are compounds with the same structural formula but different 3D arrangement of atoms

- There are two types of stereoisomerism:
  - Geometrical isomerism
  - Optical isomerism
Geometrical (cis-trans isomerism)

- Geometric isomerism involves the arrangement of groups around a double bond
  - Or a single bond that can’t rotate freely such as in a cyclic compound
- It happens because double bonds are not free to rotate
- Each C=C carbon must have two different groups attached to it.
- In the **trans** isomer, the substituents (the –CH₃ groups) are on opposite sides of the double bond
- In the **cis** isomer, the substituents are on the same side of the double bond
Cis vs Trans

- Ring structures like C=C restrict rotation and therefore can result in cis and trans isomers

 cis-1,2-dichlorocyclopropane  trans-1,2-dichlorocyclopropane
Physical Properties

- The chemical properties of geometrical isomers tend to be similar but their physical properties are different.

![Chemical structures of cis and trans 1,2-dichloroethane](image)

- Cis: polar
- Trans: non-polar
E/Z Isomers

- More general way of naming isomers

- Cahn-Ingold-Prelog priority
  - Give priority to atoms attached to the C=C bond that have the highest atomic number
Z = same side for highest molecular masses

E = opposite sides for highest molecular masses
Optical Isomers

- Optical isomerism is present in all compounds that contain at least one asymmetric (chiral) carbon atom
- An asymmetric carbon atom has four different atoms or groups attached
Optical Isomers

An optically active compound can rotate the plane of polarized light as it passes through a solution of the compound. Optical isomers are enantiomers. Enantiomers are non-superimposeable mirror images of each other. Diastereomers are not mirror images of each other.
Enantiomers

While these structures may look identical, in three dimensions they are mirror images of each other. Such molecules are called enantiomers.

If a molecule has a plane of symmetry it will not exhibit optical isomerism.
Polarized Light

Optical isomers rotate the plane of plane-polarized light in opposite directions
Racemic Mixture

A racemic mixture (or racemate) is a mixture of two enantiomers in equal amounts and is optically inactive.

Racemic Mixtures

- Equal quantities of $d$- and $l$- enantiomers.
- Notation: $(d,l)$ or $(\pm)$
- No optical activity.
- The mixture may have different boiling point (b. p.) and melting point (m. p.) from the enantiomers!
Diastereomers

- Cis-trans isomers are diastereomers
- Arise from presence of more than one chiral center
- Physical and chemical properties are different for each

Diastereomers

Wedge out of the page (toward you)
Dash in the page (away from you)
Properties

- Chemical and physical properties will often be similar but there can be important differences as you are about to see....
Key Points

- Cis isomers: the substituents are on the same side

- Trans isomers: the substituents are on opposite sides

- Cis alkenes have lower mp/bp than trans due to ‘rounder’ shape

- Cis halogenoalkenes have higher mp/bp due to polarity

- Chemical properties can be different where cis brings groups close enough to react