Homologous Series
- Definition: a series of compounds of the same family, with the same general formula and differ from one another by a common structural unit.
- Varying carbon backbone lengths, from C₁ to C₆, increasing by CH₂.
- Similar chemical properties as same functional groups present.
- There is a gradual and progressive change in physical properties.
  - E.g. Boiling Points → as the size of a molecule increases, the size of a random instantaneous dipole increases, hence the strength of LDFs increase as you ascend a homologous series. Therefore, more energy is required to break the stronger intermolecular force.

Identifying Compounds
- Identify longest carbon chain first [e.g. C₂H₅CH(CH₃)₂CH₂CH₃, longest chain is 4 (and I multiply)]
  - It is something - butane
- Bonding → all single bonds → one, double = -ene, one-triple -yn-
- Check functional group [see detailed list on next page]
  1. Alkene C=C → -ene
  2. Alkane C-C → -ane
  3. Alcohol C-OH → -ol
  4. Carboxylic Acid C₃H₂O₂H → α-Hydroxy acid
  5. Haloalkane C₂C-X → iodol/bromol/chlorofluoro-
  6. Aldehyde C=H [at chain end] → -al
  7. Ketone C=O → C=O → → → -one
  8. Amide C-N → -amide [if at end]
  9. Amino C-N → -amino

- Put numbers: e.g. alcohols → position of OH → prop-1-ol, alkenes, position of C=C, prop-1-ene.
  - Haloalkanes → position of halogen(s), 1-bromo propane.
Example: CH₃CH₂CH₂NH₂CH₃(1)(1)CH₃CH₂CH₂CH₂NH₂(1)(1)CH₃
- Let's draw it:
  - 2-amino
  - 3,3-dichloro
  - 2-ethyl

longest chain = 6 C₆
Functional Groups

1) Alkane-Alkene \( \text{C} = \text{C} \rightarrow \text{alkenyl} \)
2) Alkyne \( \text{C} = \text{C} \rightarrow \text{alkynyl} \)
3) Alcohol \( \text{C} - \text{OH} \) - hydroxyl
4) Ether \( \text{R} - \text{O} - \text{R} \) - oxy(alkane), where alkane is \( \text{R} \), e.g. ethoxyethane
5) Ketone \( \text{C} = \text{C} \rightarrow \text{none} \)
6) Aldehyde \( \text{C} = \text{O} \) - al
7) Carboxylic acid \( \text{C}^{\text{O}} \text{OH} \)
8) Ester \( \text{C} - \text{O} - \text{C} \)
9) Nitrile \( \text{C} = \text{N} \) - nitrile (alkane including last carbon = nitrile) 
8) Amine \( \text{C}^{\text{N}} \text{NH} \) - amine (alkane - amide), e.g. propanamide
9) Arene \( \text{R} \) - benzene, e.g. methyl benzene

Homologous series differ by a \( \text{CH}_2 \)

If we have a compound with 2 functional groups, example: an ethane with 2 hydroxyl groups, then it is ethane-1,2-diol. So we keep the alkane bit
Alkanes
- comprised purely of C-C and C-H bonds
- only react in presence of energy source because of relatively high bond enthalpies
- Nonpolar because of low electronegativity difference
- Low reactivity due to inability to attract other species, no double bonds or -ve/ +ves
- Undergo combustion, cracking + halogenation

Combustion:
The C=O bond in CO₂ and O-H bonds in H₂O are stronger than C-H and C-C bonds in alkanes, hence -ΔH₂O: exothermic and releases energy → used as fuel source
- Complete or Incomplete [because of insufficient O₂]
  - CH₄ + 2O₂ → CO₂ + 2H₂O [Complete]
  - CH₄ + ³/₂O₂ → [CO] + 2H₂O [Incomplete]
  - CH₄ + O₂ → [C] + 2H₂O [carcinogenic and binds to haemoglobin to reduce ability to absorb O₂]

Haloxygenation
- occurs by free radical substitution
  1. Initiation
     - Note: UV needed
     \[ \text{Cl} + \text{CH₄} \rightarrow \text{Cl}^* \text{ or } \text{Cl}_2 (g) \rightarrow 2\text{Cl}^* \]
     - homolytic fission: electrons in covalent bond equally shared

2. Propagation = forming more radicals
   1. \[ \text{Cl}^* + \text{H}-\text{C} - \text{H} \rightarrow \text{H}^\cdot + \text{HCl} \]
   - methyl radical, v. reactive
   2. \[ \text{H}^\cdot + \text{Cl}-\text{Cl} \rightarrow \text{H}-\text{C} - \text{Cl}^* \text{ then step } 2 \text{ repeated} \]
   - chloromethane
   3. \[ \text{Termination } \rightarrow \text{two radicals react} \]
      - \[ \text{H}^\cdot + \text{Cl}^* \rightarrow \text{H} + \text{Cl}_2 \text{ or } \text{H} - \text{C}^* + \text{C}^3\text{H}_4 \rightarrow \text{H} - \text{C} - \text{C} - \text{H}_2 \]
Theoretically, we can go further.

\[ \text{H}_2\text{C}-\text{Cl} + \text{Cl}^- \rightarrow \text{H}_2\text{C}-\text{Cl} + \text{HCl} \]

\[ \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl} \]

Overall = \text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}

**Nucleophilic Substitution**

- Nucleophile = an electron rich species, such as a Lewis base or ligand, attracted to +ve nuclei
- Attracted to \( \text{C}^- \) on a polar bond. E.g. \( \text{H}^+ \text{C}^- \text{E}^- \)
- Halo(Nucleophile) donates a pair of electrons to the \( \text{C}^- \text{F} \) bond, whose electrons make a half-formed bond to the halogen and nucleophile. A covalent bond is formed between them, a covalent bond;

**Diagram of a substitution by OH⁻ [Sn2 Mechanism]**

What has been explained relates to an **Sn2** mechanism.

- **Sn2** mechanism:
  - rate = \( k[\text{nucleophile}][\text{haloalkane}] \)

However, what if we have loads of stabilised? Consider the structures of haloalkanes:

- Primary
- Secondary
- Tertiary

Alkyl groups have an inductive effect, where electrons move and can stabilise a charge.
Note: $S_N2$ faster than $S_N1$, needs protic solvent to stabilize carbocation.

**Tertiary Structures**

Unimolecular $S_N2$

Most likely to undergo $S_N2$, because more stable, $R^2$.

$$\text{Br}_2 + \text{CH}_3\text{CH}=\text{CH}_2 \rightarrow \text{BrCH}_2\text{CH} = \text{CH}_2$$

**Carbocation:** The charge on the carbon is stabilized by the inductive effect of the methyl group, making it more likely to collide with $\text{OH}^-$.

**Secondary halohalanes can undergo $S_N1$ or 2. To determine, check nucleophile.** If rapid, choose $S_N2$; if not, $S_N1$. Use apotic solvent to favor $S_N2$, because it creates non-polar conditions. Aprotic solvents favor $S_N1. \text{H}_2\text{O}$ or ethanol support breakdown into carbanions, associate into $\text{H}_2\text{O}^+$ and $\text{OH}^-$. The latter is more stable, why $\text{C}$ on carbocation.

**Rates of Reaction**

The rate of reactions with haloalkanes vary with the alkane's identity. For example:

$I < \text{Br} < \text{Cl} < F$. This is because $C-I < C-\text{Br} < C-\text{Cl} < C-F$ in terms of bond strength. A lower bond strength to be broken requires less energy, resulting in a relatively lower $E_a$, $\therefore$ rate of nucleophilic substitution.

The electron density of the nucleophile also affects the rate. A lower electron density, greater attractive force between nucleophile and $\text{CH}_3$ carbon, $\therefore$ rate of reaction. $\text{OH}^-$ with anion, as it is a negatively charged molecule. This is why $\text{OH}^-$ is better nucleophile than $\text{H}_2\text{O}$, because it has a higher electron density.

$S_N2$ is also generally slower than $S_N1$, because it is a bimolecular EDS, unlike $S_N1$.

**Protonic vs Aprotic**

Aprotic for $S_N2$ — this is because protic solvents, i.e., polar solvents, will solvate the nucleophile, rendering it unable to attack the species. Also, because aprotic, no $\text{OH}^-$ to stabilize charge on carbocation, $\therefore$ unlikely to move through $S_N2$.

$S_N2$: Aprotic solvate metalation, $\therefore$ nucleophile is unsolvated, increasing rate.
Alkenes

- Unsaturated hydrocarbons containing a $\text{C} = \text{C}$ bond
- $\text{C} = \text{C}$, each $\text{C}$ is sp$^2$ hybridised
- More reactive than alkanes because of the double bond, whose constituent $\text{C}$-$\text{C}$ bond can easily be broken to create 2 new bonding positions
- Distinguishing alkenes from alkanes → burn them, alkenes produce a smoky flame, indicates an unsaturated molecule OR try decolourising bromine, happens – alkenes, not alkanes

(Hydrogenation) [Addition reaction]

- Alkenes react with hydrogen at $T \geq 150^\circ C$ in the presence of a nickel catalyst to form alkanes

\[
\begin{align*}
\text{H}_2 + \text{C} = \text{C} - \text{H} + \text{H}_2 & \rightarrow \text{H}_2 \text{C} = \text{C} - \text{H} \\
\text{C}_3\text{H}_4 + \text{H}_2 & \rightarrow \text{C}_3\text{H}_6 \\
\text{but (1)ene + hydrogen gas} & \rightarrow \text{butane}
\end{align*}
\]

- Used to break down oils containing many unsaturated hydrocarbons into saturated compounds with higher bp and mp. Allows for margarine to be solid at room temperature

(Halogenation) [Addition reaction]

- React with diatomic halogens to produce dihalogeno-compounds
- Occur at r. temperature, decolourises one halogen – tests for presence of $\text{C} = \text{C}$

\[
\begin{align*}
\text{H}_2 \text{C} = \text{C} - \text{H} + \text{Br}_2 & \rightarrow \text{H}_2 \text{C} - \text{C} - \text{H} \\
\text{C}_3\text{H}_4 + \text{Br}_2 & \rightarrow \text{C}_3\text{H}_4 \text{Br}_2
\end{align*}
\]

(prop)ene + bromine $\rightarrow$ 1, 2 dibromo-propane

(Addition Reactions with Hydrogen Halides) [Hydrohalogenation]

- React to form haloalkanes at r. temperature

\[
\begin{align*}
\text{C} = \text{C} + \text{HBr} & \rightarrow \text{C} - \text{C} - \text{H} \\
\text{ethene} + \text{hydrogen bromide} & \rightarrow \text{bromoethane}
\end{align*}
\]
Reacting with group VII, because of decreasing H-X bond enthalpy, $\Delta E_a$.

**Hydrogenation** (addition reaction)
- Reaction with H₂O to form alcohol using concentrated HCl.

$$C = C + H_2SO_4 \rightarrow (\text{H} - C - \text{C} - \text{H}) + H_2O \rightarrow \text{H} - C - \text{C} - \text{OH} + H_2SO_4$$

Ethene, sulfuric acid, ethyl hydrogen sulfate, ethanolsulfonic acid.

Overall: $\text{C}_2 \text{H}_4 + H_2O \rightarrow \text{C}_2 \text{H}_5\text{OH}$.

Need steam as well, ethanol needed as a process solvent.

**Polymerisation**
- A series of addition reactions between identical alkenes.
- Alkenes called the monomers.

$$\sum \left[ C = C \right] \rightarrow \left[ C - C \right]_n$$

$n$ ethylenes $\rightarrow$ polyethylene (polythene).

$$\sum \left[ \text{H} - C = \text{C} - \text{H} \right] \rightarrow \left[ \text{H} - C = \text{C} \right]_n$$

$n$ propenes $\rightarrow$ polypropene.

- Polychloroethene (PVC) $\rightarrow$

- Polytetrafluoroethylene (PTFE) $\rightarrow$
Electrophilic Addition

Electrophile: an electron deficient species that can accept electron pairs [Lewis Acid]

Why do alkynes undergo electrophilic addition?

1. C atoms are sp-hybridized, have trigonal planar shape with 120° bond angles formed. This creates an open structure which makes it easy for electrophiles to attack.

2. Jt bond = area of electron density above and below the internuclear axis, hence less associated with the nucleus, hence weak and easily broken in addition reactions.

3. Electrons in Jt bond attract electrophiles.

With a halogen

\[ H^+ + C≡C \quad + \quad Br^- \quad \rightarrow \quad H-\overset{\text{induced}}{\overset{\text{dipole-formed}}{\text{C}}} - \quad + \quad Br^- \]

Br₂ becomes polarized by e⁻ repulsion
from Jt bond, resulting in heterolytic
fission to form Br⁺ and Br⁻.
The Br⁺ is attracted to the Jt bond
and attacks it to form a carbocation.
The step is slow and the unstable
 carbocation reacts with Br⁻ to form
2, 3-dibromo butane.

With a hydrogen halide

\[ H^+ + C≡C \quad + \quad Br^- \quad \rightarrow \quad H-\overset{\text{hydrogen}}{\overset{\text{attached to the}}{\text{electron dense}}}{\overset{\text{sp}}{\text{Jt bond}}} \quad \rightarrow \quad H-\overset{\text{primary}}{\text{carbocation}} \]

\[ H \quad + \quad H \quad + \quad Br \quad \rightarrow \quad H-C-\quad + \quad Br \quad \rightarrow \quad H-C-\quad + \quad Br \]

\[ H \quad + \quad H \quad + \quad Br \quad \rightarrow \quad H-C-\quad + \quad Br \quad \rightarrow \quad H-C-\quad + \quad Br \]
Markovnikov's Rule

Asymmetric Alkenes

e.g. (1) \[ \text{H}-\text{C}-\text{C}=\text{C}-\text{H} \quad \text{or} \quad \text{H}_2\text{C}-\text{C}=\text{C}-\text{H} \]

(2) \[ \text{propene} \]

(3) \[ \text{H} \]

\[ \text{C} = \text{C} - \text{CH}_3 \]

\[ \text{CH}_3 \]

- There are 2 theoretical products.
- Consider propene + hydrogen bromide

\[ \text{H} \]

\[ \text{C} = \text{C} - \text{H} + \overset{\ddagger}{\text{HBr}} \rightarrow \]

\[ \text{Br} \]

- It depends on if the attacking electrophile is more likely to bond to C-1 or C-2

- We look for the most stable carbocation, primary < secondary < tertiary

- More alkyl groups, greater positive inductive effect by moving electrons to stabilize the positive charge. So 2 more stable as it is a secondary carbocation, more stable than the primary -> this is the major product, due to lower Ea

- Markovnikov's rule states that the H will bond to the carbon with the most hydrogen bonded to it [e.g., the adjacent one will be stabilized by more alkyl group]

- Formal Definition: The most electronegative atom of the reacting species bonds to least highly substituted carbon atom in the alkene (least alkyl)

- Inductive effect, e.g. double inductive effect

- Note: write equation in structural form \( \text{[CH}_3\text{C}[\overset{\ddagger}{\text{HBr}}][\text{CH}_3]\)
Alcohols

\[ C_n \overset{\text{H}}{\overset{\text{OH}}{\text{H}}} \]

- OH-functional group

- The \(-\text{O}-\text{H}\) bond is polar and increases the solubility of alcohols, especially ethanol, in water. However, solubility of alcohols decreases as you move down the chain, as larger proportion is non-polar.

**Combustion**

- Alcohol used as a fuel, as it combusts plentifully.

- Low probability of incomplete combustion because O is available from the OH.

- \( \text{C}_3 \overset{\text{H}}{\overset{\text{H}}{\overset{\text{OH}}{\text{H}}}} + 4\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} \)

- \( \Delta H \) becomes more exothermic as you descend the series as more moles of \( \text{CO}_2 \) produced.

**RECALL**

- Primary Alcohol: \( \overset{\text{OH}}{\overset{\text{H}}{\overset{\text{C}}{\text{R}}}} \rightarrow \text{butan-1-ol} \)

- Secondary Alcohol: \( \overset{\text{OH}}{\overset{\text{H}}{\overset{\text{C}}{\text{R}}}} \rightarrow \text{propan-2-ol} \)

- Tertiary Alcohol: \( \overset{\text{OH}}{\overset{\text{C}}{\text{R}}} \rightarrow \text{2-methylpropan-2-ol} \)
Oxidation

- Alcohols can be oxidised to aldehydes, ketones or carboxylic acids.
- Tertiary Alcohols cannot be oxidised because of the lack of individual Halons bonded to the C which is connected to the OH, hence it is difficult for it to be oxidised.
- Need a dilute potassium dichromate (K_2Cr_2O_7), which is reduced from Cr^6+ to Cr^3+

\[
\begin{align*}
\text{propan-1-ol, a primary alcohol} \\
\text{oxygen from Cr}_2\text{O}_7^{2-} & \rightarrow \text{propan-2-ol, a secondary alcohol}
\end{align*}
\]

Reflex

- A Liebig condenser placed above the set up.
- Aldehydes formed would vaporise due to the loss of a 
  H-bond, but would condense and fall back down, keeping it in contact with the oxidising agent for a prolonged period of time to increase P (second oxidation).

Distillation

- We use this if we only want the aldehyde.
- As the aldehyde has a lower bp than the alcohol, it evaporates, hence they move through a Liebig condenser at the adjacent side.

Note: The orange to green colour change is only seen if an oxidation occurs, not seen in tertiary alcohols.

To test for aldehydes, add Fehling's solution, it oxidises aldehydes to ketones, turning the solution red-brown from blue to red-brown.

Interestingly, isomers of carboxylic acids are esters.
Esterification

- A condensation reaction between a carboxylic acid and alcohol.
- The O-Hs bond to form an ester linkage and release a $H_2O$.
- It is an equilibrium, hence $H_2SO_4$ is used to shift equilibrium to the right (catalyst).
- Esters formed have low m.p. and b.p., hence can be separated by distillation.
- $H_2SO_4$ used as a dehydrating agent to shift equilibrium + lowers $E_A$ % catalyst.

Example: ethanol + propanoic acid

\[
\begin{align*}
H_3C-\overset{\text{bond forms}}{-C} & - OH \quad \xrightarrow{\text{high } T} \quad H_3C-\overset{-C}{} & - CH_3 \quad + H_2O \quad \text{ester linkage}
\end{align*}
\]

- Add $NaOH$/$Na_2CO_3$ to react with excess acid.

**Esters**
- Nomenclature: if alcohol + acid = ester, ester is alcohol, acid.
  - E.g. ethanol + propanoic acid = ethyl propanoate.
- Low m.p. and b.p. because of free hydroxyl groups, hence cannot form H-bonds and are insoluble in protic solvents.
- Used as perfumes, solvents, and artificial flavouring.

**Reduction Reactions**

- We need a reducing agent, e.g., $NaBH_4$, sodium tetrahydroborate, which forms highly unstable $H^+$ ions that act as a reducing agent.
- The $H^+$ undergoes a nucleophilic addition reaction with the electron-deficient carbon of a species.

- $NaBH_4$ can be used in protic solvents but cannot reduce carboxylic acids.
- $LiBH_4$ is more stronger, as it dissociates into more $H^+$ ions, but must be kept dry as $H^+ (aq) + H_2O (l) \rightarrow OH^- (aq) + H_2 (g)$, hence, only protic solvents, e.g., ethers.

Consider the reduction of butanal

\[
\begin{align*}
H_2C=CH_2 & \xrightarrow{NaBH_4 \text{ or } NaAlH_4} H_2C-CH_2\overset{-OH}{-} \quad \text{OR} \quad \overset{-OH}{-} \quad \text{OR} \quad \overset{-OH}{-} \\
\text{or} \quad \overset{-OH}{-} & \quad \text{OR} \quad \overset{-OH}{-} \\
\end{align*}
\]

- $\alpha$ aldehydes $\rightarrow$ primary alcohols.
- Consider the reduction of propanone

\[
\begin{align*}
\text{C} & \equiv \text{C} - H \quad \xrightarrow{OH^-} \quad \text{H}_2\text{C} - \text{C} - \text{CH}_3 \quad \rightarrow \quad \text{H}_3\text{C} - \text{C} - \text{CH}_3
\end{align*}
\]

- $\alpha$ ketone $\rightarrow$ secondary alcohol.
We can generalise the reductions as follows:

ketone \xrightarrow{\text{NaBH}_4, \text{H}_2\text{O}} \text{primary alcohol}

ketone \xrightarrow{\text{LiAlH}_4, \text{Et}_2\text{O}} \text{secondary alcohol}

Carboxylic acids are more complex, they too are reduced to primary alcohols.

Carboxylic acid \xrightarrow{\text{LiAlH}_4, \text{Et}_2\text{O}} \text{primary alcohol}

Benzene Rings

Cyclic Compounds

We have a lot of cyclic compounds in chemistry, such as cyclohexene.

\[
\text{C}_6\text{H}_{10}
\]

Benzene is a prime example, it is an aromatic. Chlorodealkylation was done to localise the \(\pi\) unsaturated hydrocarbon.

Kekulé thought benzene had this structure.

In fact, this theory has been falsified because of the 4 pieces of evidence here:

1. Low reactivity towards bromine only bromobenzene, no 1,2 dibromobenzene, unlike what is expected of a compound with 3 double bonds. Bromobenzene unstable at only 1 position.

2. Bond length: all the C-C bonds and C=C bond lengths were 0.140nm, a value between 0.154nm C-C bond and 0.134nm C=C bond, indicating resonance, as it lowers the number of electronic clouds in covalent bond, varying their strengths and therefore, their lengths.

3. Enthalpy of hydrogenation

\[
\begin{align*}
\text{C}_6\text{H}_6 & \rightarrow \Delta H = -120\text{kJmol}^{-1} \\
\text{C}_6\text{H}_6 + 3\text{H}_2 & \rightarrow \Delta H = -208\text{kJmol}^{-1}
\end{align*}
\]

This was expected to be 3 × (-120), as you need to break 3 \(\pi\) bonds. It was made stable by about 152kJmol\(^{-1}\).

This energy is the amount by which the internal energy of the benzene is reduced. This energy would have to be supplied to overcome the stability of C\(-\text{C}\) bond. Hence, it is called resonance energy.
Isomers: Only one isomer exists per compound, e.g. 1,2-dibromo benzene
- 1 isomer for every disubstituted benzene

Note: Addition reactions not favoured because it disrupts the aromatic ring of benzene (cloud of delocalized electrons/π bond conjugation), and resonance energy would be needed. Additionally, the lack of an aromatic ring decreases the stability of benzene. Hence, substitution is preferred, as they preserve the aromatic ring. Benzene is sp² hybridised.

**Electrophilic Addition Substitution**
- Benzene is attractive to electrophiles because of its aromatic ring
- High Ed at the first step disrupts the π bond conjugation (aromatic ring).

Energy

\[
\text{Energy} + \text{E} \rightarrow \text{Product}
\]

Where E is the electrophile

Consider the nitration (add NO₃⁻) of benzene

1. We form NO₃⁻ by reacting HNO₃ and H₂SO₄

\[
\text{H}^- + \text{O} = \text{O}^- + \text{H}^+ \rightarrow \text{O} = \text{N}^+ = \text{O}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}
\]

2. NO₃⁻ then is reacted with benzene at no more than 50°C, because further nitration occurs at 75°C

\[
\text{NO}_3^- \rightarrow \text{Product}
\]

The NO₃⁻ ion attacks the π electrons in the aromatic ring, hence an electron is used by the ring to form a covalent bond to the NO₃⁻. Simultaneously, the double bond N=O, splits to N⁺=O⁻. The π bond delocalisation of electrons is now broken and a positive charge is distributed amongst the benzene, forming a carbocation. A bond to hydrogen is subsequently broken, releasing a proton and the aromatic ring is restored.
Conditions
1. H$_2$SO$_4$ - catalyst. H$^+$ generated can react with hydrogen sulfide ion (HSO$_4^-$) to reform H$_2$SO$_4$
2. HNO$_3$ - source of NO$_2^-$
3. 50°C, ↑ rate, but no higher as it facilitates further nitration

Similar Reaction
- given AlCl$_3$ and Cl$_2$, form chlorobenzene

OR, with FeBr$_3$, Br$_2$ and C$_6$H$_6$, form bromobenzene

Back to Reduction
- By a reduction reaction, phenylamine [$C_6H_5NH_2$] can be formed

Overall
$C_6H_5NO_2 + H^+ \rightarrow C_6H_5NH_2 + H_2O$
Isomers

Isomers

Structural Isomers → molecules with the same molecular formula but different structural arrangements in space

Stereoisomers → molecules with the same structural formula but differ in atom arrangement

Configurational isomers interconvert between each other by breaking and reforming a bond.

Cis/Trans

- exist where there is restricted rotation around atoms
- e.g. always in alkenes because of double bond

Alkenes

- Why? π+ σ bond makes up the C=C bond, the π is formed from an overlap of 2 p orbitals which need to be on the same plane to combine. A bond rotation breaks the π bond, hence there is restricted rotation around atoms, e.g. cis-trans

\[ \text{H} \quad \text{C} = \text{C} \quad \text{H} \]
\[ \text{cis} \]
\[ \text{H} \quad \text{C} = \text{C} \quad \text{H} \]
\[ \text{trans} \]

Note: cis alkenes have higher b.p. because of inductive effects on atoms top/bottom resulting in polarity.

Cyclic Compounds (specifically disubstituted ones, e.g. 1,2 dichlorocyclobutane)

- Why?: Rotation restricted because C-C bonds are part of a ring system
  - e.g. (note, all drawn on same plane)

Trans-1,3 dichlorocyclobutane

Cis-1,3 dichlorocyclobutane

We only use cis/trans for rings systems, otherwise use E/Z or optical.


**E/Z isomerism**

- Like cis-trans, when we have atomic rotational restriction.
- But when C atoms of C=C bonded to more than 2 different molecule.

\[
\begin{align*}
E: & \quad H \quad C \quad Br \\
Z: & \quad I \quad C \quad CH_3
\end{align*}
\]

- Using the Cahn Ingold Prelog rules of priority, we decide whether we have an **E** or **Z** isomer.

1. **Identify heaviest ATOM bonded to C=C. So it is clearly In, as Mr(I) > Mr(Br).**
   - LHS: Mr(I) = 138.3, Mr(Br) = 80.9
   - RHS: Mr(Br) = 80.9, Mr(C) = 12.01

2. **Now, check RHS, Mr(Br) > Mr(C), so it is Br.**

\[
\begin{align*}
E: & \quad H \quad C \quad Br \\
Z: & \quad I \quad C \quad CH_3
\end{align*}
\]

- Different sides, so it is trans-like: **E**
- **E** is reverse of its cis implication, so trans.
- **Z** is same plane, unlike the 2 bits on the **E**.

- **E** and **Z** are written in brackets. Hence, the example would simply be
  - **(E)** - 1-iodo, 2-bromo pent-1-ene

**E vs Z**

- Different physical properties, e.g. b.p., solubility, m.p.
- Different chemical properties or different possible reactions can occur.

**Optical Isomers**

- **Enantiomers**
  - Definition: Isomers that are non-superimposable mirror images of one another.
  - A chiral carbon is required.
  - A chiral carbon is a carbon bonded to 4 different atoms or groups, also called asymmetric.
  - 2 enantiomers per optically active molecule.
  - We draw them as tetrahedrons, with the chiral carbon at the centre.
  - If asked for both enantiomers, write as the following:

\[
\begin{align*}
E: & \quad X \quad Y \\
Z: & \quad Y \quad X
\end{align*}
\]
A mixture containing a 50-50 mix of each enantiomer is a racemic mixture, and is optically inactive.

Identifying chiral carbons. Draw the enantiomers of C<sub>4</sub>H<sub>9</sub>H<sub>4</sub>Br.

We need an isomer of bromobutane that has a chiral carbon.

```
CH<sub>3</sub>       Br       NO!
\( \text{H}_3\text{C} - \text{C} - \text{CH}_3 \)
```

```
\( \text{H}_3\text{C} - \text{C} - \text{C} - \text{C} - \text{H} \)
```

```
\( \text{Br} \quad \text{Br} \quad \text{H}_3\text{C} - \text{C} - \text{C}_2\text{H}_5 \)
```

```
\( \text{C}_2\text{H}_5 \quad \text{H}_3\text{C} - \text{C} - \text{H} \)
```

All different groups, hence optically active.

Note: the wedges and dashes must be used!

Something interesting (not in syllabus)

- Distinguishing R and S optical isomers
- Look at the heaviest atom bonded heaviest atom bonded in order and number them. If 1 → 4 go clockwise, it is R, if anti clockwise then S.

Clockwise, hence it is an R isomer.

Anti clockwise, hence S.

Plane polarised light

- A transverse wave of light
- Normal light vibrates in every plane, but plane polarised light moves perpendicular to the wave. A plane polarised (Pp) light generated by shining light through a polarising filter.
- Enantiomers rotate plane polarised light. If plane polarised light passed through, the plane of polarization is rotated in opposite directions.

An X-ray chiral compound in a long glass tube.

A polarizing filter followed by an analyser that determines the rotation angle.
if we have a racemate, there is no net rotation as both chiral compounds rotate clockwise and anti-clockwise, cancelling each other out. :: not optically active

Note: naturally occurring chiral compounds are optically active, only 1 type of enantiomer

clockwise (−) enantiomer is an R isomer, anti is an S

Comparing properties of enantiomers

1. Chemical
   - different reactivities, and because biological systems (e.g. enzymes) are chiral, it has significant impacts. E.g. thalidomide: listen to "We Didn't Start the Fire,". 1 enantiomer reduced morning sickness, another caused birth defects
   - To produce a single enantiomer, asymmetric synthesis is used, a process using a chiral catalyst

2. Physical - also differ

Effect
- Distinct chemical and physical properties allow for separation
- Hence, 2 enantiomers in a racemate can be separated by "resolution."

(Su1 and Su2 w.r.t. stereoisomers)

Su1
- it is stereospecific, causes an inversion of spatial arrangement of atoms around a C atom
- Called stereospecific because the spatial arrangement of atoms in reactants determines 3D configuration of the products
- This is because bond formation is before bond cleavage in the transition state, so no loss of stereochromistry

Su2
- non stereospecific as there are 2 possible binding sites on carbocation intermediate because it is planar.

nucleophile can attack from any position in step 2
hence an S_N1 mechanism produces a racemate, as a mix of optically active isomers are produced.

Question Tips
i) Structure of benzene - Cs are sp^2 hybridised, 120° angles, hexagonal resonance, all equal C-C bonds, bond order of 1.5
Every Organic Reaction

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- Free Radical Substitution
  - UV light
    
    \[
    \text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_4 + 2\text{Cl}^- \rightarrow \text{propagation}
    \]
    
    \[
    \text{CH}_4 + \text{Cl}^- \rightarrow \text{CH}_3 + \text{HCl} \rightarrow \text{termination}
    \]
    
    \[
    \text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^- \rightarrow \text{termination}
    \]

Electrophilic Addition

- Hydrolysis → up 150°C, Nickel Catalyst, H₂(g)
- alkene to alkane

  - Reactions with interhalogen compounds / halogens [halogenation] / hydrogen halogen halide

  Hydrohalogenation

  - Hydrolysis → H₂SO₄ and H₂O

    \[
    \begin{align*}
    \text{C} & \quad \text{H} \quad \text{H} \\
    \text{H} & \quad \text{H} \quad \text{H} \\
    \end{align*}
    \]

    \[
    \begin{align*}
    \text{H} & \quad \text{C} \quad \text{C} \quad \text{OSO}_3\text{H} \\
    \text{H} & \quad \text{H} \quad \text{H} \\
    \end{align*}
    \]

    \[
    \begin{align*}
    \text{H} & \quad \text{C} \quad \text{C} \quad \text{OSO}_3\text{H} \\
    \text{H} & \quad \text{H} \quad \text{H} \\
    \end{align*}
    \]

  - Be careful with Markovnikov's rule

Nucleophilic Substitution

- SN1 if tertiary, SN2 if primary, both for secondary [product = SN1', aprotic = SN2']
- No conditions
- Convert halogen–alkanes into alcohols with a OH nucleophile

Alcohol Oxidation

- All require K₂Cr₂O₇ and H₂SO₄, an acidified potassium dichromate (VI)
- alcohol (1°) → aldehyde → carboxylic acid
  - distillation reflux
- alcohol (2°) → ketone
- alcohol (3°) → no reaction, no H₂S to be lost as part of oxidation
**Reductions**

- With LiBH₄ and H₂O/propanol solvent
  1. ketone $\rightarrow$ secondary alcohol
  2. primary aldehyde $\rightarrow$ primary alcohol
- With NaAlH₄ and aprotic solvent (because otherwise H₂ ions gone)
  1. carboxylic acid $\rightarrow$ primary alcohol
- Nitrbenzene to phenylamine

```
\begin{equation}
\text{NO}_2 + \text{H}^+ + \text{Sn} \rightarrow \text{H}_2\text{O}
\end{equation}
```

**Esterification**

- Alcohol + carboxylic acid
- H₂SO₄ catalyst + dehydrating agent (shifts equilibrium)

**Electrophilic Substitution**

- Production of nitrobenzene
  - H₂SO₄ and HNO₃ at 50°C, all conc