17. Organic Chemistry II

A2 Organic naming

**Hydrocarbon** is a compound consisting of hydrogen and carbon only

**Saturated**: Contain single carbon-carbon bonds only
**Unsaturated**: Contains a C=C double bond

**Molecular formula**: The formula which shows the actual number of each type of atom

**Empirical formula**: shows the simplest whole number ratio of atoms of each element in the compound

**General formula**: algebraic formula for a homologous series e.g. CnH2n

**Displayed formula**: shows all the covalent bonds present in a molecule

**Homologous series** are families of organic compounds with the same functional group and same general formula.
- They show a gradual change in physical properties (e.g. boiling point).
- Each member differs by CH2 from the last.
- Same chemical properties.

**Functional group** is an atom or group of atoms which when present in different molecules causes them to have similar chemical properties.

**Drawing Displayed formulae**

When drawing organic compounds add the hydrogen atoms so that each carbon has 4 bonds

**General rules for naming carbon chains**
- Count the longest carbon chain and name appropriately
- Find any branched chains and count how many carbons they contain
- Add the appropriate prefix for each branch chain

Eg -CH3 methyl or -C2H5 ethyl –C3H7 propyl

3,5-dimethylheptane

<table>
<thead>
<tr>
<th>code</th>
<th>no of carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>meth</td>
<td>1</td>
</tr>
<tr>
<td>eth</td>
<td>2</td>
</tr>
<tr>
<td>prop</td>
<td>3</td>
</tr>
<tr>
<td>but</td>
<td>4</td>
</tr>
<tr>
<td>pent</td>
<td>5</td>
</tr>
<tr>
<td>hex</td>
<td>6</td>
</tr>
<tr>
<td>hept</td>
<td>7</td>
</tr>
<tr>
<td>oct</td>
<td>8</td>
</tr>
<tr>
<td>non</td>
<td>9</td>
</tr>
<tr>
<td>dec</td>
<td>10</td>
</tr>
</tbody>
</table>

When compounds contain more than one functional group, the order of precedence determines which groups are named with prefix or suffix forms. The highest precedence group takes the suffix, with all others taking the prefix form. However, double and triple C-C bonds only take suffix form.

**Order of priority highest first**:
Carboxylic acids > carboxylic acid derivative > nitriles > aldehydes > ketones > alcohols > amines
<table>
<thead>
<tr>
<th>homologous series</th>
<th>functional group</th>
<th>prefix / suffix (* = usual use)</th>
<th>example</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkenes</td>
<td>suffix -ene</td>
<td></td>
<td>ethene</td>
</tr>
<tr>
<td>alcohols</td>
<td>suffix* -ol</td>
<td>prefix hydroxy-</td>
<td>Propan-1-ol</td>
</tr>
<tr>
<td>halogenoalkane</td>
<td>prefix chloro-</td>
<td>prefix bromo-</td>
<td>1-chloropropane</td>
</tr>
<tr>
<td>aldehydes</td>
<td>suffix* -al</td>
<td>prefix formyl-</td>
<td>ethanal</td>
</tr>
<tr>
<td>ketones</td>
<td>suffix* -one</td>
<td>prefix oxo-</td>
<td>Propanone</td>
</tr>
<tr>
<td>carboxylic acids</td>
<td>suffix -oic acid</td>
<td></td>
<td>Ethanoic acid</td>
</tr>
<tr>
<td>nitriles</td>
<td>suffix -nitrile</td>
<td>prefix cyano-</td>
<td>Propanenitrile</td>
</tr>
<tr>
<td>amines</td>
<td>suffix* -amine</td>
<td>prefix amino-</td>
<td>Propylamine Or propan-1-amine</td>
</tr>
<tr>
<td>esters</td>
<td>-yl-oate</td>
<td></td>
<td>Methyl ethanoate</td>
</tr>
<tr>
<td>Acyl chloride</td>
<td>-oyl chloride</td>
<td></td>
<td>ethanoylchloride</td>
</tr>
<tr>
<td>Amide</td>
<td>-amide</td>
<td></td>
<td>Ethanamide</td>
</tr>
</tbody>
</table>
General rules for naming functional groups

- The functional group is indicated by a prefix or suffix. e.g. chloroethane

When using a suffix, add in the following way:

If the suffix starts with a vowel - remove the –e from the stem alkane name
- Propan-1-ol, butan-1-amine, ethanoic acid, ethanoylchloride, butanamide

If the suffix starts with a consonant or there are two or more of a functional group meaning di, or tri needs to be used then do not remove the –e from the stem alkane name
- Propanenitrile, ethane-1,2-diol, propanedioic acid, propane-1,2,3-triol, Pentane-2,4-dione.

- The functional group on the carbon chain is given by a number – counting from the end of the molecule that gives the functional group the lowest number. For aldehydes, carboxylic acids & nitriles, the functional group is always on carbon 1.

- We only include numbers, however, if they are needed to avoid ambiguity.

- We only include numbers, however, if they are needed to avoid ambiguity.

- The position of the functional group on the carbon chain is given by a number – counting from the end of the molecule that gives the functional group the lowest number. For aldehydes, carboxylic acids & nitriles, the functional group is always on carbon 1.

- The functional groups take precedence over branched chains in giving the lowest number.

- Where there are two or more of the same groups, di-, tri- or tetra are used. Note the point made above about the addition of ‘e’ to the stem.

- Words are separated by numbers with dashes

- Numbers are separated by commas

- If there is more than one functional group or side chain, the groups are listed in alphabetical order (ignoring any di, tri).

The suffix for alkenes can go in front of other suffixes.

Halogenoalkanes

Class the halogen as a substituent on the C chain and use the suffix -fluoro, -chloro, -bromo, or -iodo. (Give the position number if necessary)

Alcohols

These have the ending -ol and if necessary the position number for the OH group is added between the name stem and the –ol

If the compound has an –OH group in addition to other functional groups that need a suffix ending then the OH can be named with the prefix hydroxy):

If there are two or more -OH groups then di, tri are used. Add the ‘e’ on to the stem name though.
Aldehydes
An aldehyde’s name ends in -al.
It always has the C=O bond on the first carbon of the chain so it does not need an extra number. It is by default number one on the chain.

Ketones
Ketones end in -one.
When ketones have 5C’s or more in a chain then it needs a number to show the position of the double bond. E.g. pentan-2-one.
If two ketone groups then di is put before -one and an e is added to the stem.
The prefix oxo- should be used for compounds that contain a ketone group in addition to a carboxylic acid or aldehyde.

Carboxylic acids
These have the ending -oic acid but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end.
If there are carboxylic acid groups on both ends of the chain then it is called a dioic acid.

Nitriles
These end in -nitrile, but the C of the CN group counts as the first carbon of the chain. Note the stem of the name is different: butanenitrile and not butannitrile.

Carboxylic acid derivatives
Esters have two parts to their names.
The bit ending in -yl comes from the alcohol that has formed it and is next to the single bonded oxygen.
The bit ending in -anoate comes from the carboxylic acid. (This is the chain including the C=O bond)

Amides
Secondary and tertiary amides are named differently to show the two (or three) carbon chains. The smaller alkyl group is preceded by an -N which plays the same role as a number in positioning a side alkyl chain.

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Isomers

**Structural isomers**: same molecular formula different structures (or structural formulae)

Structural isomerism can arise from
- Chain isomerism
- Position isomerism
- Functional group isomerism

**Chain isomers**: Compounds with the same molecular formula but different structures of the carbon skeleton

![pentane](image1)

2-methylbutane

2,2-dimethylpropane

**Position isomers**: Compounds with the same molecular formula but different structures due to different positions of the same functional group on the same carbon skeleton

![1-bromopropane](image2)

2-bromopropane

**Functional group isomers**: Compounds with the same molecular formula but with atoms arranged to give different functional groups

![ethanol](image3)

Methoxymethane: an ether

Cyclohexane - cyclo alkane

hexene - alkene

Aldehydes and ketones of the same chain length would be classed as functional group isomers - e.g. Propanal and propanone (both C₃H₆O)

Stereoisomerism

**Definition: Stereoisomers** have the same structural formulae but have a different spatial arrangement of atoms

There are two types of **stereoisomerism**: geometrical (E-Z isomerism) and optical isomerism

Alkenes can exhibit a type of isomerism called **E-Z stereoisomerism**

E-Z isomers exist due to restricted rotation about the C=C bond

Single carbon-carbon covalent bonds can easily rotate

E-Z stereoisomers arise when:
(a) There is restricted rotation around the C=C double bond.
(b) There are two different groups/atoms attached both ends of the restricted double bond
But-1-ene is a structural isomer of But-2-ene but does not show E-Z isomerism

Naming E-Z stereoisomers

On both sides of the double bond determine the priority group

Priority Group: The atom with the bigger A is classed as the priority atom

If the priority atom is on the same side of the double bond it is labelled Z from the German zusammen (The Zame Zide!)

If the priority atom is on the opposite side of the double bond it is labelled E from the German entgegen (The Epposite side!)

17A Optical Isomerism

Optical isomerism occurs in carbon compounds with 4 different groups of atoms attached to a carbon (called an asymmetric carbon).

These four groups are arranged tetrahedrally around the carbon.

A mixture containing a 50/50 mixture of the two isomers (enantiomers) is described as being a racemate or racemic mixture.

Many naturally occurring molecules contain chiral C atoms, but are usually found in nature as a pure enantiomer

Different systems of nomenclature are in existence for optical isomers. D/L or +/− are commonly used, but both have been superseded by the more useful and informative R/S system (this is not on the syllabus – for information only).

One optical isomer will rotate light clockwise (+) (called dextrorotatory). The other will rotate it anticlockwise (−) (called laevorotatory).

A racemic mixture (a mixture of equal amounts of the two optical isomers) will not rotate plane-polarised light.

Two compounds that are optical isomers of each other are called enantiomers.

Optical isomers have similar physical and chemical properties, but they rotate plane polarised light in different directions.

One enantiomer rotates it in one direction and the other enantiomer rotates it by the same amount in the opposite direction.

A carbon atom that has four different groups attached is classed as a chiral (asymmetric) carbon atom.

This causes two different isomers that are not superimposable to be formed. They are mirror images.
Chemical Reactions and Optical Isomers

Formation of a racemate

A racemate will be formed in a reaction mechanism when a trigonal planar reactant or intermediate is approached from both sides by an attacking species.

Nucleophilic addition of HCN to aldehydes and ketones (unsymmetrical) when the trigonal planar carbonyl is approached from both sides by the HCN attacking species: results in the formation of a racemate.

Formation of a racemate with SN$_1$ mechanism

The Br first breaks away from the haloalkane to form a planar carbocation intermediate.

The OH$^-$ ion can then attack from either side resulting in different enantiomers and a racemate forms.

Because a racemate forms there will be no optical activity in the products.

Comparison with SN$_2$ mechanism

In the SN$_2$ mechanism no intermediates are formed and the reaction occurs via a transition state.

If the reactant was chiral then during the reaction the opposite enantiomer would form.

The product will rotate light in the opposite direction to the reactant.

A racemate can also be formed in the AS reaction of the electrophilic addition of HBr to an unsymmetrical alkene.

The bromide can attack this planar carbocation from both sides leading to a racemate.

If the alkene is unsymmetrical, addition of hydrogen bromide can lead to isomeric products.

Major product 90%

Minor product 10%
Compounds with C=O group

17B Carboxyls: Aldehydes and Ketones

Carbonyls are compounds with a C=O bond. They can be either aldehydes or ketones.

If the C=O is on the end of the chain with an H attached it is an aldehyde. The name will end in -al.

If the C=O is in the middle of the chain it is a ketone. The name will end in -one.

Solubility in water

The smaller carbonyls are soluble in water because they can form hydrogen bonds with water.

Reactions of carbonyls

In comparison to the C=C bond in alkenes, the C=O is stronger and does not undergo addition reactions easily.

The C=O bond is polarised because O is more electronegative than carbon. The positive carbon atom attracts nucleophiles.

Oxidation Reactions

Potassium dichromate K₂Cr₂O₇ is an oxidising agent that causes alcohols and aldehydes to oxidise.

Oxidation of Aldehydes

Key point: Aldehydes can be oxidised to carboxylic acids, but ketones cannot be oxidised.

Full Equation for oxidation

₃CH₃CHO + Cr₂O₇²⁻ + 8H⁺ → ₃CH₃CO₂H + 4H₂O + 2Cr³⁺

Tollen’s reagent

Reagent: Tollen’s Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of [Ag(NH₃)₂]⁺.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Tollen’s reagent into a carboxylic acid and the silver(I) ions are reduced to silver atoms.

Observation: with aldehydes, a silver mirror forms coating the inside of the test tube. Ketones result in no change.

CH₃CHO + 2Ag⁺ + H₂O → CH₃COOH + 2Ag + 2H⁺

Fehling’s solution

Reagent: Fehling’s solution containing blue Cu²⁺ ions.

Conditions: heat gently

Reaction: aldehydes only are oxidised by Fehling’s solution into a carboxylic acid and the copper ions are reduced to copper(I) oxide.

Observation: Aldehydes: Blue Cu²⁺ ions in solution change to a red precipitate of Cu₂O. Ketones do not react.

₃CH₃CHO + 2Cu²⁺ + 2H₂O → CH₃COOH + Cu₂O + 4H⁺
Reduction of carbonyls

**Reagents:** LiAlH$_4$ in dry ether

**Conditions:** Room temperature and pressure

**Type of reaction:** Reduction

**Role of reagent:** Reducing agent

Reducing agents such as NaBH$_4$ (sodium tetrahydridoborate) or LiAlH$_4$ (lithium tetrahydridoaluminate) will reduce carbonyls to alcohols.

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**Addition of hydrogen cyanide to carbonyls to form hydroxynitriles**

**Reaction:** carbonyl $\rightarrow$ hydroxynitrile

**Reagent:** HCN in presence of KCN

**Conditions:** Room temperature and pressure

**Mechanism:** nucleophilic addition

When naming hydroxy nitriles the CN becomes part of the main chain

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**Reaction of carbonyls with iodine in presence of alkali**

**Reagents:** Iodine and sodium hydroxide

**Conditions:** warm very gently

The product CH$I_3$ is a yellow crystalline precipitate with an antiseptic smell

Only carbonyls with a methyl group next to the C=O bond will do this reaction. Ethanal is the only aldehyde that reacts. More commonly is methyl ketones.

This reaction is called the Iodoform test

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\[
\text{CH}_3\text{COCH}_3 + 3\text{I}_2 + 4\text{NaOH} \rightarrow \text{CHI}_3 + \text{CH}_3\text{COONa} + 3\text{NaI} + 3\text{H}_2\text{O}
\]

\[
\text{CH}_3\text{COCH}_2\text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \rightarrow \text{CHI}_3 + \text{CH}_3\text{CH}_2\text{COONa} + 3\text{NaI} + 3\text{H}_2\text{O}
\]
The melting point of the crystal formed can be used to help identify which carbonyl was used. Take the melting point of orange crystals product from 2,4-DNP. Compare melting point with known values in database.

Reaction with 2,4-dinitro phenylhydrazine

2,4-DNP reacts with both aldehydes and ketones. The product is an orange precipitate. It can be used as a test for a carbonyl group in a compound.

Use 2,4-DNP to identify if the compound is a carbonyl. Then to differentiate an aldehyde from a ketone use Tollen’s reagent.

The melting point of the crystal formed can be used to help identify which carbonyl was used. Take the melting point of orange crystals product from 2,4-DNP. Compare melting point with known values in database.

17C Carboxylic Acids

Acidity
The carboxylic acid are only weak acids in water and only slightly dissociate, but they are strong enough to displace carbon dioxide from carbonates.

\[
\text{CH}_3\text{CO}_2\text{H}(aq) \rightleftharpoons \text{CH}_3\text{CO}_2\text{⁻}(aq) + \text{H}^+(aq)
\]

Solubility in Water
The smaller carboxylic (up to C4) acids dissolve in water in all proportions but after this the solubility rapidly reduces. They dissolve because they can hydrogen bond to the water molecules.

Hydrogen bonding in solid ethanoic acid
Hydrogen bonding between dimer in solid ethanoic acid

Solid ethanoic appears to have Mr of 120

Delocalisation
The carboxylic acid salts are stabilised by delocalisation, which makes the dissociation more likely.

The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.

The pi charge cloud has delocalised and spread out. The delocalisation makes the ion more stable and therefore more likely to form.
Strength of carboxylic acids

Increasing chain length pushes electron density on to the COO⁻ ion, making it more negative and less stable. This makes the acid less strong.

Propanoic acid less acidic than ethanoic acid

Electronegative chlorine atoms withdraw electron density from the COO⁻ ion, making it less negative and more stable. This makes the acid more strong.

Chloroethanoic acid more acidic than ethanoic acid

Methods of preparing carboxylic acids

Full Oxidation of Primary Alcohols

Reaction: primary alcohol → carboxylic acid
Reagent: potassium dichromate(VI) solution and dilute sulfuric acid
Conditions: use an excess of dichromate, and heat under reflux: (distil off product after the reaction has finished)

Observation: the orange dichromate ion (Cr₂O₇²⁻) reduces to the green Cr³⁺ ion

Oxidation of Aldehydes

Reaction: aldehyde → carboxylic acid
Reagent: potassium dichromate (VI) solution and dilute sulfuric acid.
Conditions: heat under reflux

Full Equation for oxidation
3CH₃CHO + Cr₂O₇²⁻ + 8H⁺ → 3 CH₃COOH + 4H₂O + 2Cr³⁺

Hydrolysis of Nitriles

Reaction: Nitrile → carboxylic acid
Reagent: dilute hydrochloric/ sulfuric acid.
Conditions: heat under reflux

CH₃CH₂CN + H⁺ + 2H₂O → CH₃CH₂COOH + NH₄⁺
The Reactions of Carboxylic Acids

Reduction of carboxylic acids to alcohols
Lithium tetrahydridoaluminate (LiAlH₄) is a strong reducing agent.
Reagents: LiAlH₄ in dry ether
Conditions: Room temperature and pressure
Type of reaction: Reduction
Role of reagent: Reducing agent

Carboxylic acids will be reduced to primary alcohols

\[
\begin{array}{c}
\text{H}_2\text{C} = \text{C} = \text{O} + 4\text{[H]} \rightarrow \text{H}_2\text{C} = \text{C} = \text{O} - \text{O} - \text{H} + \text{H}_2\text{O} \\
\text{Propanoic acid} \rightarrow \text{Propan-1-ol}
\end{array}
\]

Salt formation reactions of carboxylic acids
Carboxylic acids can form salts with metals, alkalis and carbonates.

\[
\begin{align*}
\text{acid} + \text{metal (Na)} & \rightarrow \text{salt} + \text{hydrogen} \\
2\text{CH}_3\text{CO}_2\text{H} + 2\text{Na} & \rightarrow 2\text{CH}_3\text{CO}_2\text{Na}^+ + \text{H}_2 \\
\text{acid} + \text{alkali (NaOH)} & \rightarrow \text{salt} + \text{water} \\
\text{CH}_3\text{CO}_2\text{H} + \text{NaOH} & \rightarrow \text{CH}_3\text{CO}_2\text{Na}^+ + \text{H}_2\text{O} \\
\text{acid} + \text{carbonate (Na}_2\text{CO}_3) & \rightarrow \text{salt} + \text{water} + \text{CO}_2 \\
2\text{CH}_3\text{CO}_2\text{H} + \text{Na}_2\text{CO}_3 & \rightarrow 2\text{CH}_3\text{CO}_2\text{Na}^+ + \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]

The effervescence caused by production of CO₂ with carboxylic acids with solid Na₂CO₃ or aqueous NaHCO₃ can be used as a functional group test for carboxylic acids.

Oxidation of methanoic acid
Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group.

\[
\text{H}-\text{C} = \text{O} + [\text{O}] \rightarrow \text{H}-\text{O}-\text{C} = \text{O} - \text{H}
\]

It forms carbonic acid (H₂CO₃) which can decompose to give CO₂.

Reaction of carboxylic acid with phosphorous (V) chloride
Reaction: carboxylic acid → acyl chloride
Reagent: PCl₅ phosphorous(V)chloride
Conditions: room temp

\[
\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}
\]

This reaction with PCl₅ (phosphorous(V)chloride) can be used as a test for carboxylic acids. You would observe misty fumes of HCl produced.

\[
\begin{array}{c}
\text{H}_3\text{C} - \text{C} = \text{O} + \text{PCl}_5 \rightarrow \text{H}_3\text{C} - \text{C} = \text{O} + \text{POCl}_3 + \text{HCl}
\end{array}
\]
Esterification

Carboxylic acids react with alcohols, in the presence of a strong acid catalyst, to form esters and water.

$$\text{Carboxylic Acid} + \text{Alcohol} \xrightarrow{H^+} \text{Ester} + \text{water}$$

Esters have two parts to their names, eg methyl propanoate.

The bit ending in –anoate comes from the carboxylic acid and includes the C in the C=O bond.

The bit ending in –yl comes from the alcohol that has formed it and is next to the single bonded oxygen.

Uses of Esters

Esters are sweet smelling compounds that can be used in perfumes and flavourings.

Esters can be used as solvents for polar organic substances

Ethyl ethanoate is used as a solvent in glues and printing inks

Esters can have pleasant smells

For use in perfumes they need to be non toxic, soluble in solvent such as ethanol, volatile (turns into gas easily), and not react with water.

Hydrolysis of esters

Esters can be hydrolysed and split up by either heating with acid or with sodium hydroxide.

i) with acid reagents: dilute acid (HCl)
conditions: heat under reflux

$$\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{H^+} \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}$$

This reaction is the reverse reaction of ester formation. When an ester is hydrolysed a carboxylic acid and an alcohol are formed.

This reaction is reversible and does not give a good yield of the products.

ii) with sodium hydroxide reagents: dilute sodium hydroxide
conditions: heat under reflux

$$\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2^– \text{Na}^+ + \text{CH}_3\text{OH}$$

methyl propanoate sodium propanoate methanol

The carboxylic acid salt product is the anion of the carboxylic acid. The anion is resistant to attack by weak nucleophiles such as alcohols, so the reaction is not reversible.

Uses of Esters

Although polar, they do not form hydrogen bonds (reason: there is no hydrogen bonded to a highly electronegative atom) thus, they have much lower b.p. than the hydrogen-bonded carboxylic acids they came from. They are also almost insoluble in water.
Carboxylic acid derivatives: Acyl Chlorides

Acyl Chlorides

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

ethanoyl chloride

Acyl chlorides are much more reactive than carboxylic acids

The Cl group is classed as a good leaving groups (to do with less effective delocalisation.) This makes acyl chlorides and acid anhydrides much more reactive than carboxylic acids and esters

**Reaction with water**

Change in functional group: **acyl chloride → carboxylic acid**
Reagent: water
Conditions: **room temp.**

\[
\text{RCOCl} (l) + \text{H}_2\text{O} \rightarrow \text{RCO}_2\text{H} + \text{HCl} (g)
\]

\[
\text{CH}_3\text{C} = \text{OCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{HCl} (g)
\]

Observation: Steamy white fumes of HCl are given off

**Reaction with alcohol**

Change in functional group: **acyl chloride → ester**
Reagent: **alcohol**
Conditions: **room temp.**

\[
\text{RCOCI} (l) + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{RCO}_2\text{CH}_2\text{CH}_3 + \text{HCl} (g)
\]

\[
\text{CH}_3\text{C} = \text{OCl} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{C} = \text{OCH}_2\text{CH}_3 + \text{HCl}
\]

Observation: Steamy white fumes of HCl are given off

This reaction for making esters is much better than using carboxylic acids as the reaction is much quicker and it is not a reversible reaction

**Reaction with ammonia**

Change in functional group: **acyl chloride → primary amide**
Reagent: **ammonia**
Conditions: **room temp.**

\[
\text{RCOCI (l)} + 2\text{NH}_3 \rightarrow \text{RCONH}_2 + \text{NH}_4\text{Cl} (s)
\]

\[
\text{CH}_3\text{C} = \text{OCl} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{C} = \text{O}\text{NH}_2 + \text{NH}_4\text{Cl} (s)
\]

Observation: white smoke of NH\(_4\)Cl is given off

**Reaction with primary amines**

Change in functional group: **acyl chloride → secondary amide**
Reagent: **primary amine**
Conditions: **room temp.**

\[
\text{RCOCI} + 2\text{CH}_3\text{NH}_2 \rightarrow \text{RCONHCH}_3 + \text{CH}_3\text{NH}_3\text{Cl}
\]

\[
\text{CH}_3\text{C} = \text{OCl} + 2\text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{C} = \text{ONHCH}_3 + \text{CH}_3\text{NH}_3\text{Cl}
\]

N-methylethanamide

N-Goalby chemrevise.org
Polyesters

There are two types of polymerisation: addition and condensation

Condensation Polymerisation

The two most common types of condensation polymers are polyesters and polyamides which involve the formation of an ester linkage or an amide linkage.

In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g. H₂O or HCl.

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di carboxylic acid, diol, diacyl chloride.

Forming polyesters uses these reactions we met earlier in the course

Carboxylic Acid + Alcohol → Ester + water  Acyl chloride + Alcohol → Ester + HCl

If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:

dicarboxylic acid + diol → poly(ester) + water  diacyl dichloride + diol → poly(ester) + HCl

Using the carboxylic acid to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous HCl fumes.

Terylene- a common polyester

Benzene-1,4-dicarboxylic acid

Terylene fabric is used in clothing, tire cords

The -1 here is because at each end of the chain the H and OH are still present

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Chemical reactivity of condensation polymers

Polyesters can be broken down by hydrolysis and are, therefore, biodegradable.

The reactivity can be explained by the presence of polar bonds which can attract attacking species such as nucleophiles and acids.

Polymers can be hydrolysed by acid and alkali.
With HCl a polyester will be hydrolysed and split up into the original dicarboxylic acid and diol.
With NaOH an polyester will be hydrolysed and split up into the diol and dicarboxylic acid salt.

It is also possible for polyamides and polyesters to form from one monomer, if that monomer contains both the functional groups needed to react.

2-hydroxypropanoic acid (lactic acid)

3 repeating units

4-hydroxypentanoic acid

It is possible for some of these compounds to form various cyclic esters under different conditions from forming the polymer.
You do not need to learn these but may be asked to deduce structures from information given.