OCR A Chemistry A-level

Module 6.1: Aromatic Compounds, Carbonyls and Acids

Detailed Notes

6.1.1 Aromatic Compounds

Benzene and Aromatic Compounds

Arenes are aromatic compounds that **contain a benzene ring as part of their structure**.

Benzene is an **arene** consisting of a ring of **six carbon atoms** each bonded to **one hydrogen atom**, giving it the molecular formula C_6H_6. This structure means benzene has a ring of **delocalised electrons**:

Example: Displayed and skeletal formula of benzene

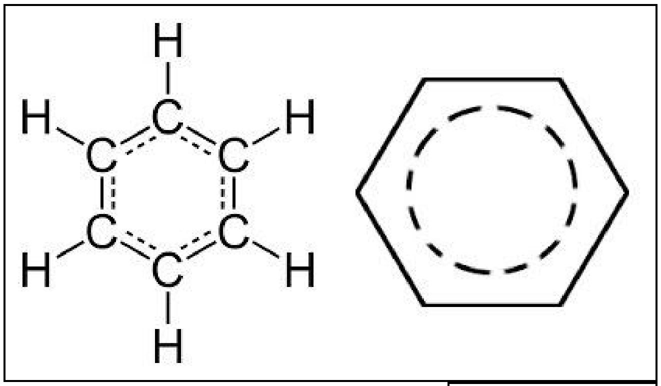


Image courtesy of Quora

The outer electron from the **p-orbital** of each carbon atom is **delocalised** into the centre to form the central ring. This overlap of electrons results in the formation of **π-bonds**.

The delocalised ring structure makes benzene **very stable** compared to other molecules of a similar size.

Evidence for Benzene’s structure

When benzene was first discovered its structure was unknown. It was predicted from empirical measurements that it had a structure similar to that of **cyclohexatriene**, with three double bonds and three single bonds. However, chemical evidence and experiments suggested benzene actually had the structure given above.

Example: Displayed formula of cyclohexatriene

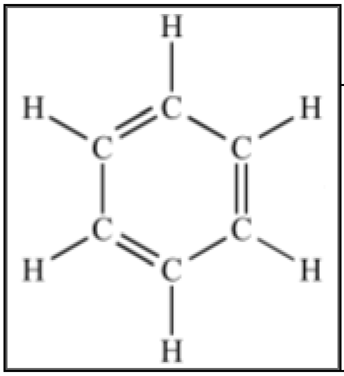


Image courtesy of www.chem.ucla.edu

Thermochemical Evidence - Cyclohexatriene vs. Benzene

Based on the structure of cyclohexatriene, the enthalpy change of hydrogenation for benzene was **predicted to be -360 kJ mol^{-1}**, three times the enthalpy change of cyclohexene.

Example:

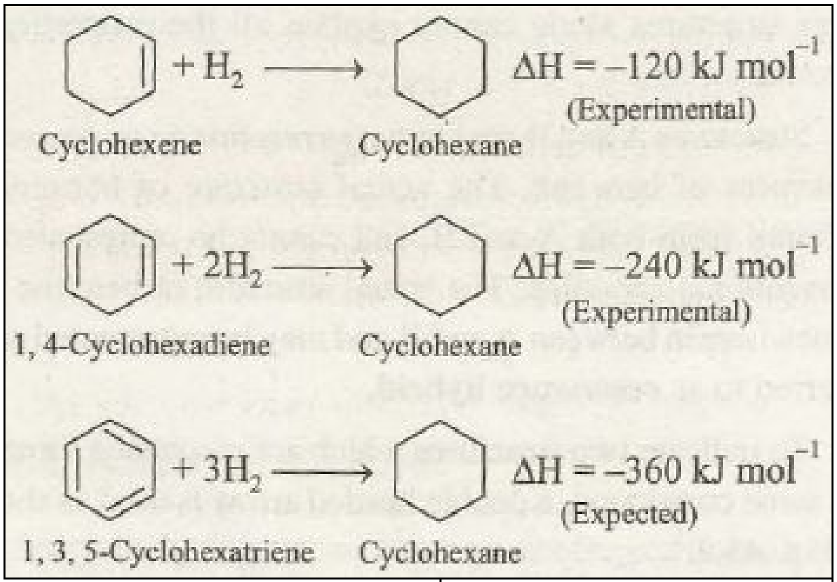


Image courtesy of chemistry-assignment.com

It was later discovered that the enthalpy change of hydrogenation of benzene was **actually -208 kJ mol^{-1},** leading to the conclusion that its **structure** was **different** to that of **cyclohexatriene**. The enthalpy change of hydrogenation was **less negative than expected** (less exothermic), indicating that benzene is more stable than the suggested cyclohexatriene structure predicts.

X-ray Diffraction and Infrared Data

X-ray diffraction experiments have shown that **all** the bond lengths between carbon atoms in benzene are **the same**. If the cyclohexatriene structure was correct, three of the bond lengths would be the length of a **single** carbon bond and three would be the length of a **double** carbon bond. In reality, each bond in the benzene ring has an **intermediate length** in between that of a double and single bond.

The cyclohexatriene structure also did not explain **infrared data** collected from benzene molecules.

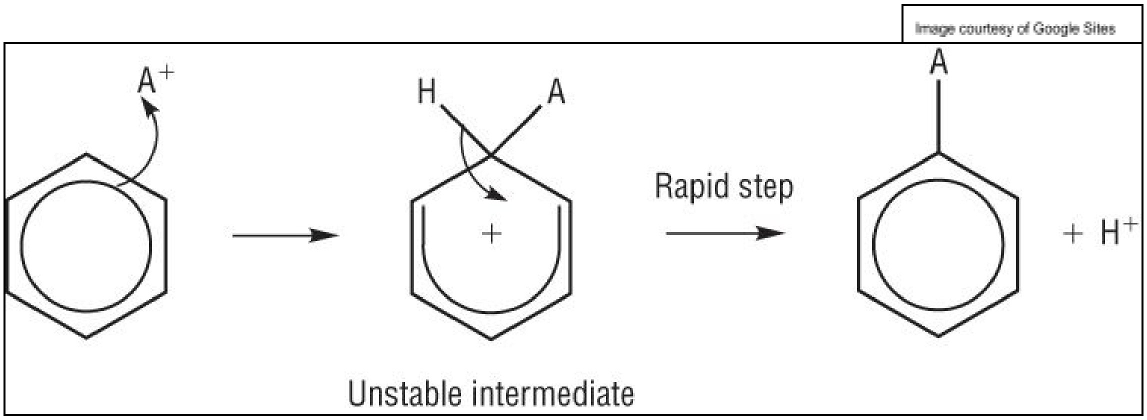
Electrophilic Substitution

Benzene is resistant to **electrophilic addition** reactions, such as bromination, which other compounds with carbon-carbon double bonds, such as **alkenes**, readily undergo. Benzene does not undergo electrophilic addition since this would involve breaking up the **stable** delocalised ring of electrons. Benzene instead undergoes **electrophilic substitution** reactions.

Electrophilic Substitution

The delocalised ring in benzene is an **area of high electron density,** making it susceptible to attack from **electrophiles**. In an electrophilic substitution mechanism, electrophiles attack the electron ring, **partially destroying** it, before it is then restored to form the aromatic product. This mechanism allows **aromatic amines** and **nitrobenzene** to be produced from benzene.

Mechanism - General electrophilic substitution mechanism



The electrophile is shown as A$^+$.

Halogenation

Halogenation is a type of **electrophilic substitution reaction** in which benzene reacts with halogens in the presence of a **catalyst,** such as iron(III) bromide ($FeBr_3$). The catalyst is required to generate the electrophile, which then reacts as shown above.

Iron(III) bromide acts as a **halogen carrier** in the halogenation reaction. Other examples of halogen carriers include iron, iron halides, and aluminium halides.

Example: The iron(III) bromide polarises the bromine molecule. This makes it easier for the bromine bond to break so that the bromine atom can act as an electrophile.

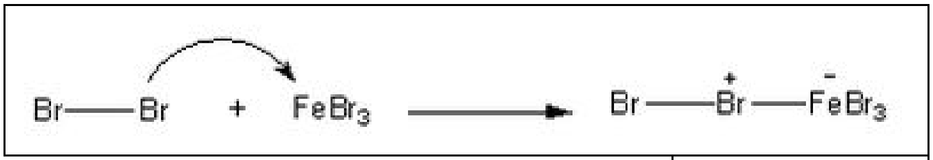


Image courtesy of wikipedia

Nitration

Nitration is a form of electrophilic substitution, where the electrophile is an **NO_2^+ ion**. This is a **reactive intermediate**, produced in the reaction of concentrated sulfuric acid (H_2SO_4) with concentrated nitric acid (HNO_3). Sulfuric acid behaves as a **catalyst** since it is not used up in the reaction.

Example: Formation of the electrophile

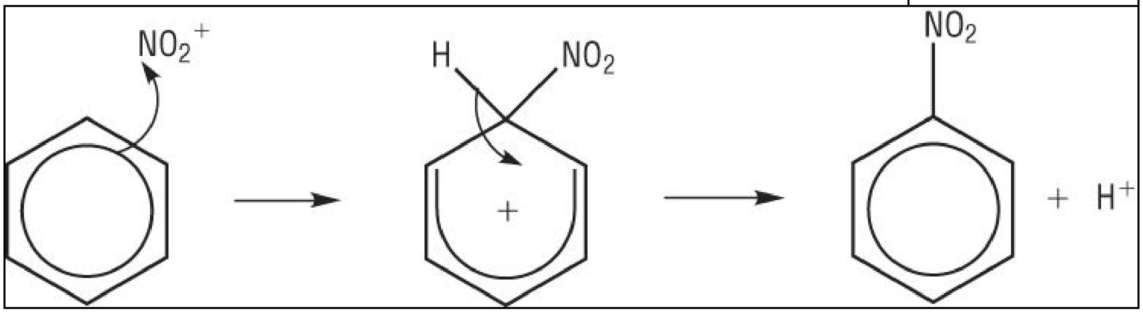
$$H_2SO_4 + HNO_3 \longrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ \longrightarrow H_2O + \boxed{NO_2^+}$$

When heated with benzene, these reagents lead to the **substitution of the NO_2^+ electrophile** onto the benzene ring, **replacing a hydrogen** atom. The hydrogen ion released reacts with the HSO_4^- (produced above) to **reproduce** the sulfuric acid **catalyst**.

Mechanism

Image courtesy of Socratic



This reaction shows the **mono-substitution** of a single NO_2^+ electrophile, which takes place when the reaction temperature is **55°C**. At temperatures greater than this, multiple substitutions can occur on the benzene ring. It is vital that only one substitution occurs for the production of **aromatic amines**.

Friedel-Crafts Acylation

The delocalised electron ring in benzene can also act as a **nucleophile**, leading to their nucleophilic **attack on acyl chlorides**. This reaction is known as **Friedel-Crafts acylation**.

In order for the reaction to take place, a **reactive intermediate** must be produced from a reaction between the acyl chloride and an **aluminium chloride catalyst**.

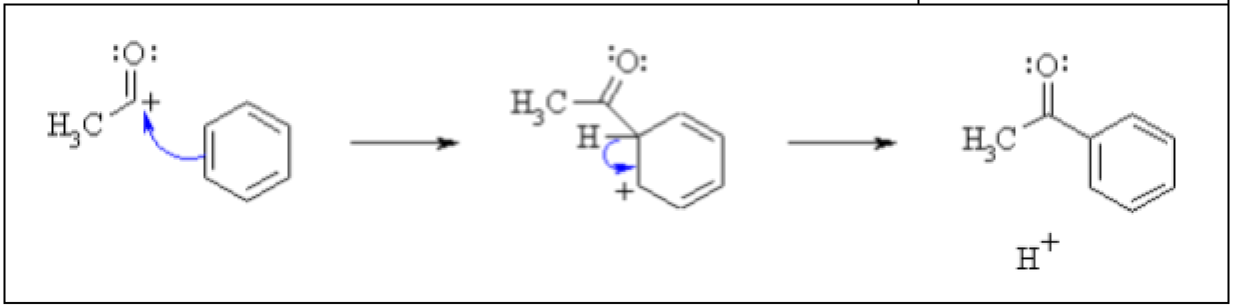
Example: Formation of the reactive intermediate

$$\text{R-COCl} + \text{AlCl}_3 \longrightarrow \boxed{\text{R-CO}^+} + \text{AlCl}_4^-$$

This reactive intermediate is then attacked by the benzene ring.

Mechanism

Image courtesy of the University of Calgary



At the end of the reaction, the **H^+ ion** removed from the ring reacts with the **$AlCl_4^-$ ion** to reform the aluminium chloride, indicating it to be a **catalyst**. It also releases steamy fumes of HCl gas.

The product of this reaction is a **phenylketone**. In this case, the benzene group is called a **phenyl group**. These molecules are commonly used in the industrial production of dyes, pharmaceuticals and even explosives.

Bromine Water

The **test for unsaturation** would be expected to work for benzene like it does for alkenes, however, benzene is resistant to bromination. This is due to the **delocalised electron density** of the π-system in benzene compared with the localised electron density of the π-bond in alkenes. The delocalised model makes benzene relatively stable and hence not reactive enough to decolourise bromine water.

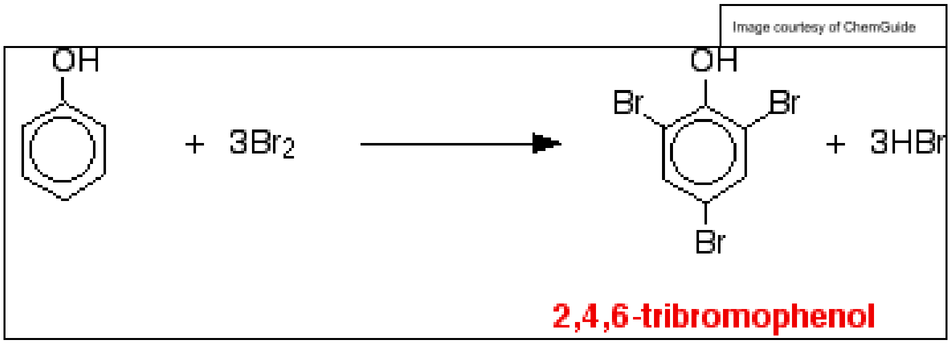
Phenols

Phenols are organic compounds containing a **benzene ring** with an OH **alcohol group**. This makes them **aromatic alcohols**. Phenols are weak acids. They can be neutralised in a reaction with NaOH but will not react with carbonates.

Electrophilic Substitution Reactions

Phenol, an aromatic compound with the formula **C_6H_5OH**, is produced in electrophilic substitution reactions with benzene. Phenol can react with bromine water via **multiple substitutions** to produce 2,4,6-tribromophenol which forms as a **white precipitate** with a distinct smell of antiseptic. This reaction decolourises bromine water.

Example: Formation of 2,4,6-tribromophenol



Benzene, on the other hand, cannot react with bromine water. The increased reactivity of phenol is due to the **lone pair of electrons on the oxygen atom,** which is delocalised into the benzene ring structure. This increases the **electron density** of the ring, making it less stable and thus **more susceptible to attack** from electrophiles.

The electrophilic substitution reaction of phenol with **dilute nitric acid** will form a mixture of **2-nitrophenol and 4-nitrophenol**. Nitration with phenol does not require concentrated HNO_3 or the presence of a concentrated H_2SO_4 catalyst due to the **increased reactivity** of phenol in comparison to benzene. The NO_2 group is electron withdrawing so decreases the electron density of the ring and stabilises the product. As a result, at room temperature, only one substitution will occur.

Directing Effects

Electron donating groups such as OH and NH_2 **direct electrophiles** to substitute at the **2-** and **4-** positions. Electron-withdrawing groups such as NO_2 are **3-directing** in electrophilic substitution of aromatic compounds. These effects occur to favour the most stable charged intermediate.

In the example above, it can be seen that the 2/4-directing OH group causes bromine to substitute at these positions only.

Directing effects can be used to predict substitution products. This is very important in organic synthesis as it allows you to control the structure of the products.

6.1.2 Carbonyl Compounds

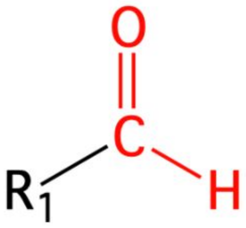
Carbonyl compounds are organic compounds containing a **carbonyl group,** C=O. This gives them the functional group **-CO**. The most common carbonyl compounds are **aldehydes and ketones**.

The functional group allows these molecules to form **hydrogen bonds** with water. A hydrogen bond forms between a lone **electron pair** on the oxygen atom and a **∂+ region** on a hydrogen atom. Aldehydes and ketones are, therefore, **soluble in water.**

However, because aldehydes and ketones themselves do not have a ∂+ hydrogen atom, they do **not** form hydrogen bonds between molecules. The only type of intermolecular force which exists between their molecules are **van der Waals forces**.

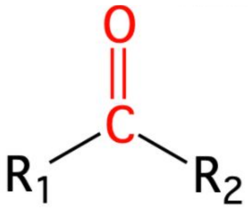
Aldehydes

Aldehydes are produced from the initial oxidation and distillation of **primary alcohols**. Aldehydes have a carbonyl group on a carbon atom at the **end of the carbon chain** (only attached to **one other carbon atom**). This gives them the functional group **-CHO**.



Ketones

Ketones are recognised by the **functional group -C=O,** a carbonyl group. They are produced from the oxidation of **secondary alcohols** with acidified potassium dichromate(VI). Ketones have a carbonyl group on a carbon atom that is attached to **two other carbon atoms**.



Reactions of Carbonyl Compounds

Oxidation

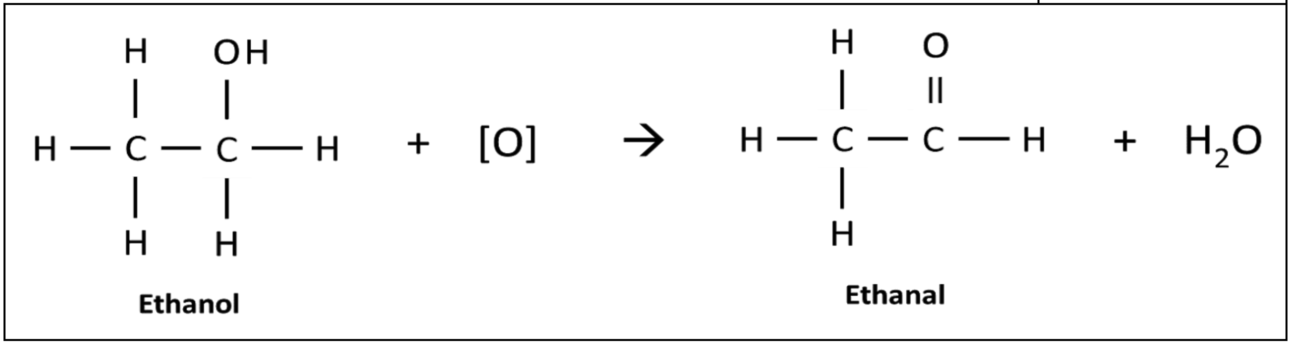
Primary and secondary alcohols can be **oxidised** to produce various products, but **tertiary** alcohols are **not easily oxidised**.

In equations for organic redox reactions, **[O]** and **[H]** should be used in place of the oxidising and reducing agents respectively.

Primary alcohols can be heated in the presence of **acidified potassium dichromate(VI)** and **immediately distilled** to produce **aldehydes**. The reagents used are $K_2Cr_2O_7$ and H_2SO_4. The oxidising agent is the dichromate ion, $Cr_2O_7^{2-}$.

Example:

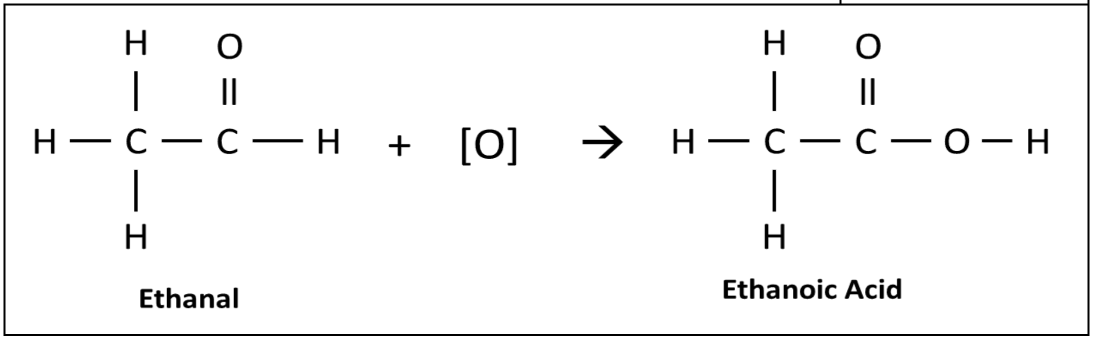
Image courtesy of anhourofchemaday


Ethanol
Ethanal

When heated under **reflux** conditions, primary alcohols will be **oxidised further** to produce **carboxylic acids**.

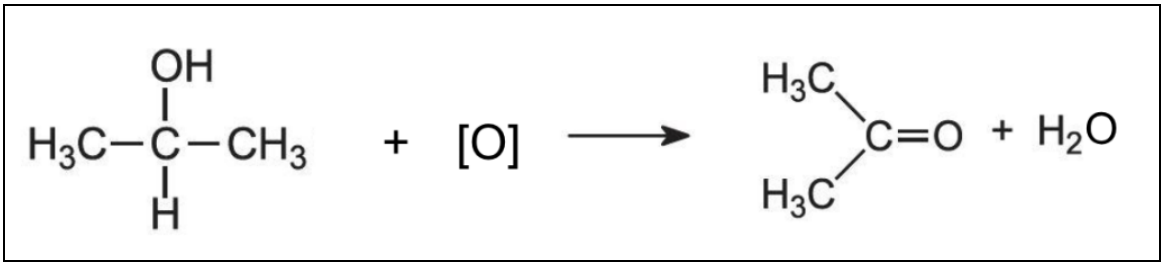
Example:

Image courtesy of anhourofchemaday


Ethanal
Ethanoic Acid

Secondary alcohols can be oxidised to **ketones** when heated in the presence of **acidified potassium dichromate(VI).**

Example:



Potassium Dichromate(VI) ($K_2Cr_2O_7$)

Potassium dichromate(VI) is used as an **oxidising agent** in the oxidation of alcohols. As the alcohol is oxidised, potassium dichromate(VI) is **reduced**. This reduction is observed as a colour change from **orange to green**, which indicates the alcohol has undergone oxidation. The colour change occurs due to the change in **oxidation state** of the chromium ion.

Example:

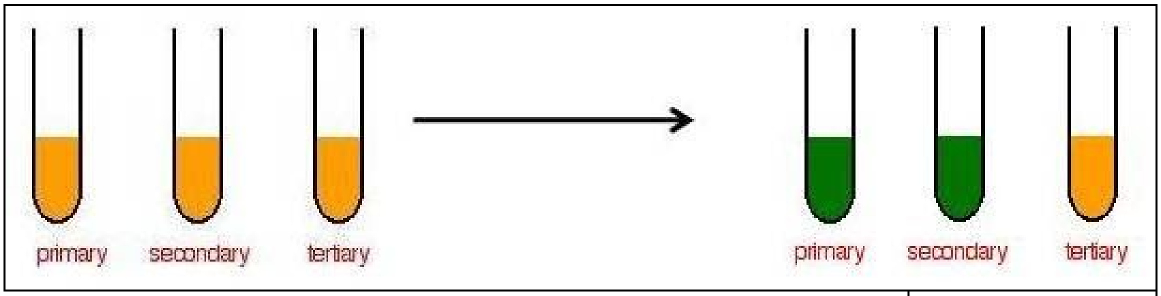


Image courtesy of chemhume.co.uk

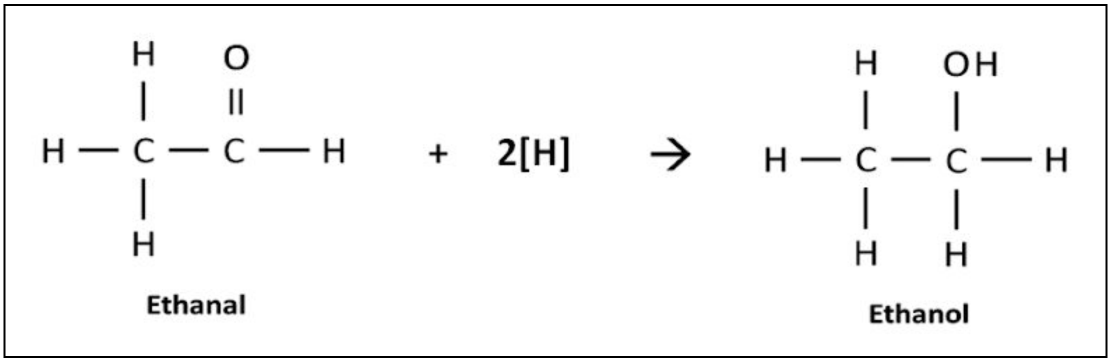
Nucleophilic Addition

All of the oxidation reactions involved in the production of carbonyl compounds from alcohols can be **reversed via reduction reactions**.

In these reactions, a **reducing agent** of sodium borohydride, **$NaBH_4$**, is used. The reaction is an example of **nucleophilic addition**.

The reducing agent $NaBH_4$ provides the **$H:^-$ nucleophile**. First a salt is formed, and then a dilute acid is added to release the alcohol from the salt. The reducing agent can be represented by **[H]** in the chemical equation.

Example:



Nucleophilic addition reactions can also take place with the **:CN⁻ nucleophile**. This is used in **chemical synthesis** as it causes the carbon chain to be **extended** by one carbon atom. The product of the reaction is a **hydroxynitrile**.

Mechanism

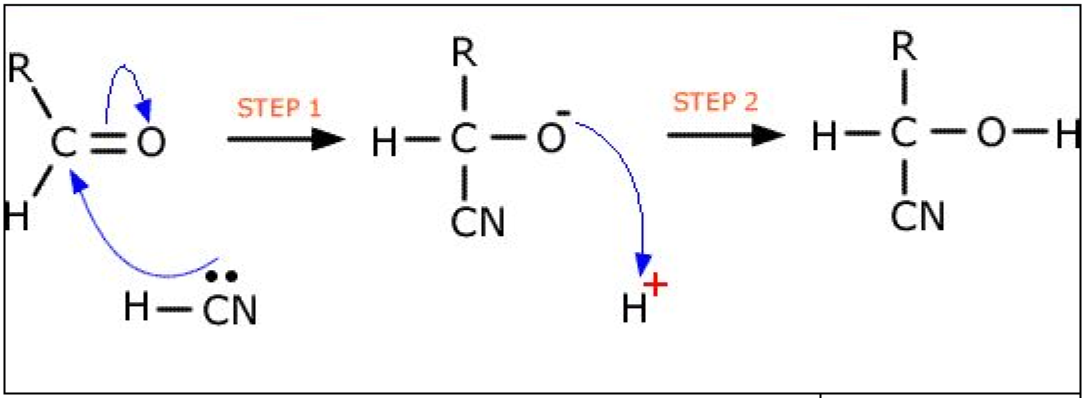


Image courtesy of Get Revising

NaCN (sodium cyanide) is often used as the reagent along with a H^+ source to provide the **HCN** (hydrogen cyanide). This is because HCN is **hard to store** and is a toxic gas which reacts to produce **dangerous byproducts**.

Hydroxynitriles commonly contain a **chiral carbon centre** meaning optical isomers of the product are produced. The :CN- nucleophile can attack from either above or below the **planar double bond**, causing different **enantiomers** to be produced.

The mechanism for nucleophilic addition with $NaBH_4$ is the same as the mechanism above, except it uses $H:^-$ as the nucleophile.

Characteristic Tests for Carbonyl Compounds

2,4-dinitrophenylhydrazine (2,4-DNPH) Test

2,4-DNPH can be used as a qualitative test for the carbonyl functional group. When aldehydes and ketones are reacted with 2,4-DNPH a **yellow**, **orange** or **reddish-orange** precipitate will form; the exact colour depends on the identity of the compound. Alcohols and other molecules which don't contain carbonyl groups do not produce a precipitate.

Carbonyl compounds and their derivatives have **sharp melting points**, meaning they melt over a narrow range of temperatures. These compounds can have their melting points determined experimentally and their values compared to a **databook** to identify them.

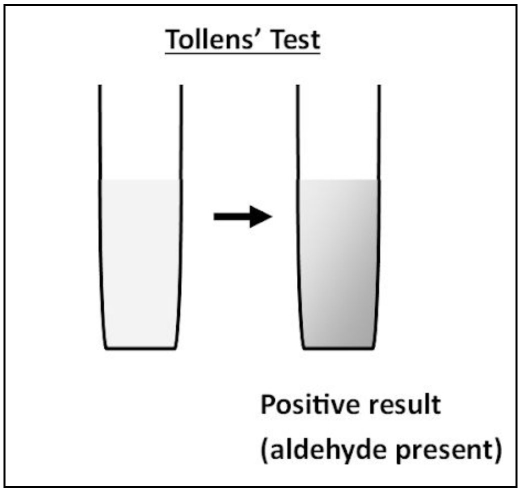
2,4-DNPH can be used to identify specific aldehydes/ketones by use of melting point data. The 2,4-DNPH is added to the compound so that a precipitate forms. The solid is then purified by **recrystallisation**. The melting point of the pure crystals formed can then be compared with the melting points of **2,4-dinitrophenylhydrazones** of all the common aldehydes and ketones.

Tollen's Test

Aldehydes can be identified using **Tollen's reagent.** If Tollen's reagent is added to an aldehyde, a layer of silver will form on the walls of the test tube. If a **ketone** is present the solution will remain **colourless**.

Tollens reagent is **ammoniacal silver nitrate**. It oxidises the aldehyde to a carboxylic acid and reduces silver ions to silver in the presence of an aldehyde. The silver can be seen deposited on the edge of the test tube. This is sometimes described as a **silver mirror**.

Example:

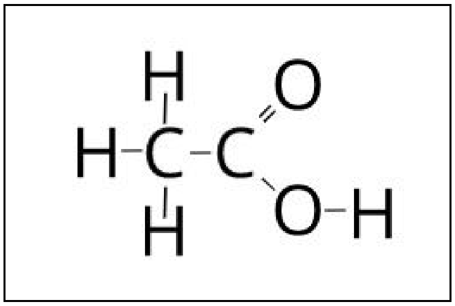


6.1.3 Carboxylic Acids and Esters

Properties of Carboxylic Acids

Carboxylic acids are organic compounds identified by the **functional group -COOH,** which contains a **carbonyl group (C=O)** and an **-OH acid group**. When naming carboxylic acids, the suffix **-anoic acid** is used. For example, a carboxylic acid containing a chain of four carbon atoms would be called butanoic acid.

Example: The displayed structure of ethanoic acid.



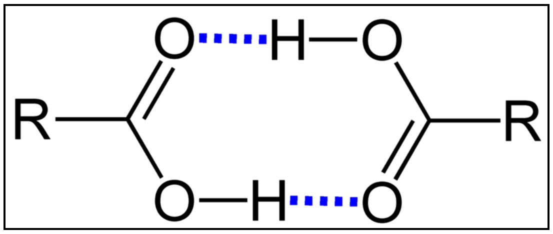
Carboxylic acids can be prepared by the **oxidation** of primary alcohols or aldehydes under **reflux**. Acidified potassium dichromate(VI) is commonly used as the oxidising agent. They can also be produced by the **hydrolysis** of **nitrile compounds**.

Properties

The **-COOH functional group** allows carboxylic acid molecules to form hydrogen bonds between each other. They can also form hydrogen bonds **with water,** meaning they are **soluble in water**. As chain length increases, their solubility decreases since CH_2 groups do not form hydrogen bonds with water and add bulk to the compound.

Since carboxylic acids can form **hydrogen bonds** between molecules, with both the C=O and O-H parts of the functional group, their boiling and melting points are even **higher** than those of alcohols, aldehydes and ketones.

Example: Hydrogen bonding between two carboxylic acid molecules.



Reactions of Carboxylic Acids

Carboxylic acids are **weak acids** and therefore react with bases in a **neutralisation** reaction to produce a **salt.**

Example:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

$$CH_3CH_2COOH + NH_3 \rightarrow CH_3CH_2COONH_4$$

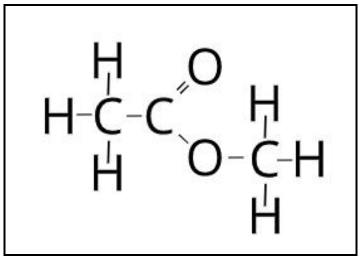
(ammonia propanoate)

The reaction of a **metal** with a carboxylic acid will produce the corresponding **salt** and **hydrogen** gas. Whereas, the reaction with a **metal carbonate** will produce the **salt, carbon dioxide and water**.

Esters

Esters have the functional group **-COO-**. They are named after the **alcohol and carboxylic acid** from which they are formed. For example, the ester formed from methanol and propanoic acid is methyl propanoate and the ester formed from butanol and ethanoic acid is butyl ethanoate.

Example: The displayed structure of methyl ethanoate.



Esterification

Carboxylic acids can **react with alcohols** in the presence of a **strong acid catalyst** to form **esters**. **Concentrated sulfuric acid** is often used as the acid catalyst. This reaction is called **esterification** and is carried out under **reflux**.

Example:

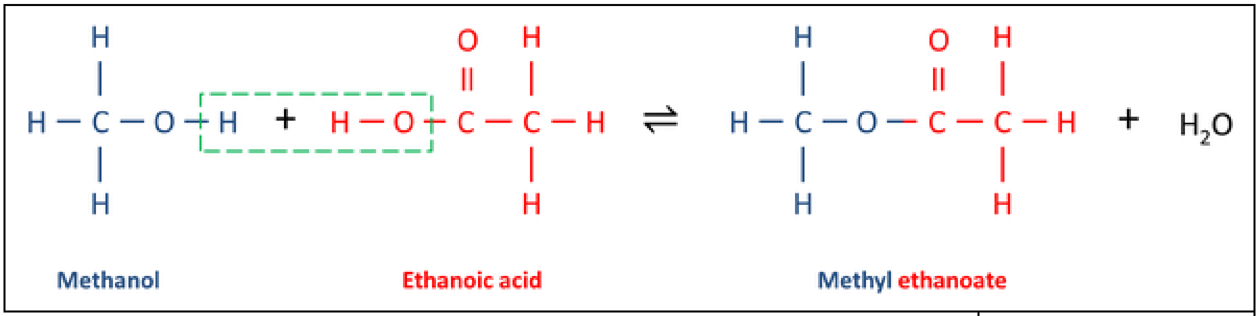


Image courtesy of anhourofchemaday

A method for remembering the reaction: Remove the -OH from the acid and the hydrogen from the alcohol to make water. Then join the acid and alcohol together.

Esters are **sweet-smelling compounds** used in food flavourings and perfumes. They have **low boiling points** and make **good solvents** for polar molecules.

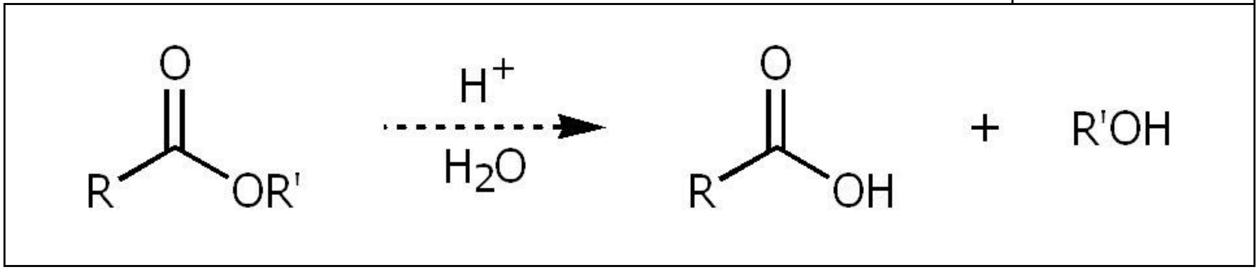
Acid anhydrides can also be used to esterify alcohols. This occurs in an **addition-elimination** mechanism. Acid anhydrides react less vigorously than acyl chlorides and do not produce toxic HCl as a side product. As a result, they are often preferred as a reagent in esterification.

Hydrolysis of Esters

Ester hydrolysis is the **reverse reaction** to esterification, converting esters back into alcohols and carboxylic acids. This process is done by **adding water,** but can be carried out under **different conditions** to produce different products.

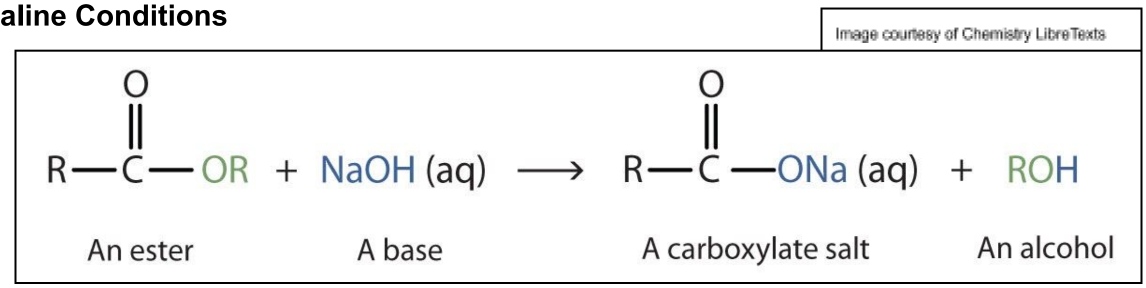
Acidic Conditions

Image courtesy of SlidePlayer



The reaction conditions are hot aqueous acid. This produces a simple reverse reaction back to the alcohol and carboxylic acid.

Alkaline Conditions



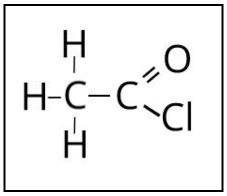
The reaction conditions are hot aqueous alkali. The carboxylic acid produced reacts further with the base to form a salt, so the final products are the carboxylate salt and alcohol.

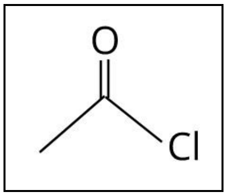
The process of producing this salt is called **saponification**. Salts such as these are commonly used as **soaps** because they have **hydrophilic and hydrophobic** properties.

Acyl Chlorides

Acyl chlorides have the functional group **-COCl** and have the suffix **-oyl chloride**, with the stem of their name representing the longest chain of carbon atoms.

Example: The displayed structure and skeletal structure of ethanoyl chloride.

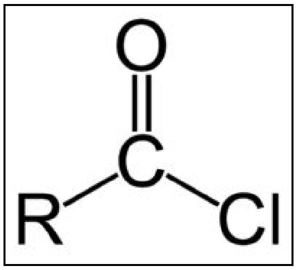




Acylation

Carboxylic acids have **derivative molecules** where the -OH group is replaced by another group. **Acyl Chlorides** are one such derivative that reacts violently due to the **very polar -COCl group**.

Example: Functional group of acyl chlorides



Acyl chlorides can be produced by the reaction between carboxylic acids and **$SOCl_2$**.

Example:

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$

Reactions of Acyl Chlorides

The -COCl group makes acyl chlorides very reactive and so they react with a wide range of molecules to give a wide range of products:

+ Water → Carboxylic Acid

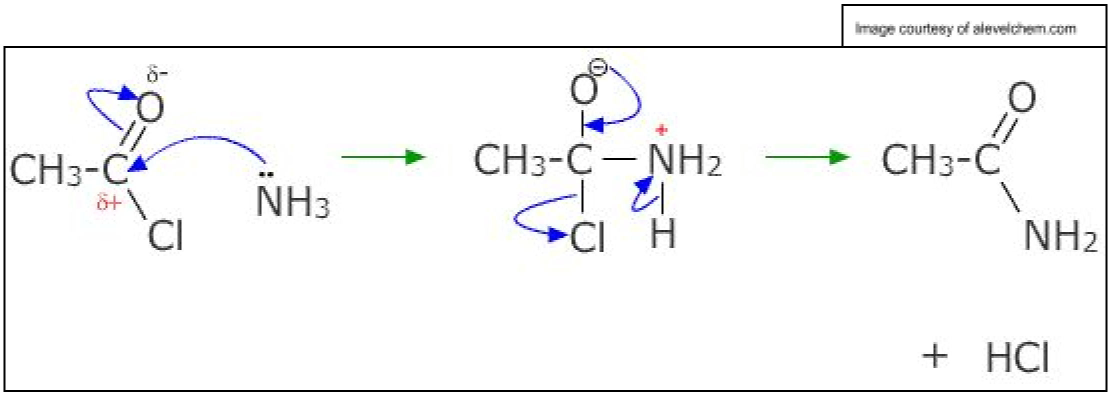
+ Alcohol → Ester

+ Ammonia → Amide

+ Amines → N-substituted Amide

Acyl chlorides react via **nucleophilic addition-elimination reactions**. In these reactions, the addition of a nucleophile leads to the elimination of a product under **aqueous conditions**. The mechanism for the reaction of ethanoyl chloride with ammonia is shown below:

Example: Nucleophilic addition-elimination mechanism



Acyl chlorides can be used in the **esterification of phenol**, which is not readily esterified by carboxylic acids.