OCR (B) Chemistry A-level

Storyline 10: Colour by Design

Detailed Notes

Bonding and Structure

Dyes and Chromophore

Dyes are coloured compounds which work by chemically bonding themselves to a substrate, dyes must absorb light in the **visible spectrum** by having at least one **chromophore** and a **conjugated system**. A chromophore is an atom or chemical group which is responsible for the colour of a compound. Some chemical functional groups are able to **modify** the chromophore, -OH, $-NH_2$ or $-NR_2$ are added to alter the colour of the compound. These groups change the colour of a compound by having a pair of electrons which can join the delocalised electron system.

Functional Groups which affect Bonding of Dyes

Dyes are designed for a specific substrate. To make sure they bond together well, they need to have a high affinity to each other. Dyes attach themselves to fibers by **intermolecular forces** (hydrogen bonding and Van der Waals), **covalent bonds** and **ionic bonds**. The fibers which dyes bond to have specific groups to allow this to occur, in polymers such as nylon and wool the slightly basic -NH group of the amide links are attracted to the -COOH and $-SO_3H$ groups of dyes. -OH groups also allow hydrogen bonding to occur between the dyes and fibers.

Functional Groups which affect the Solubility of Dyes

The most common groups used to alter the **solubility** of a dye are **auxochromes** e.g. carboxylic acid, sulfonic acid, amino and hydroxyl groups. The solubility of a dye is an important parameter to control in industry.

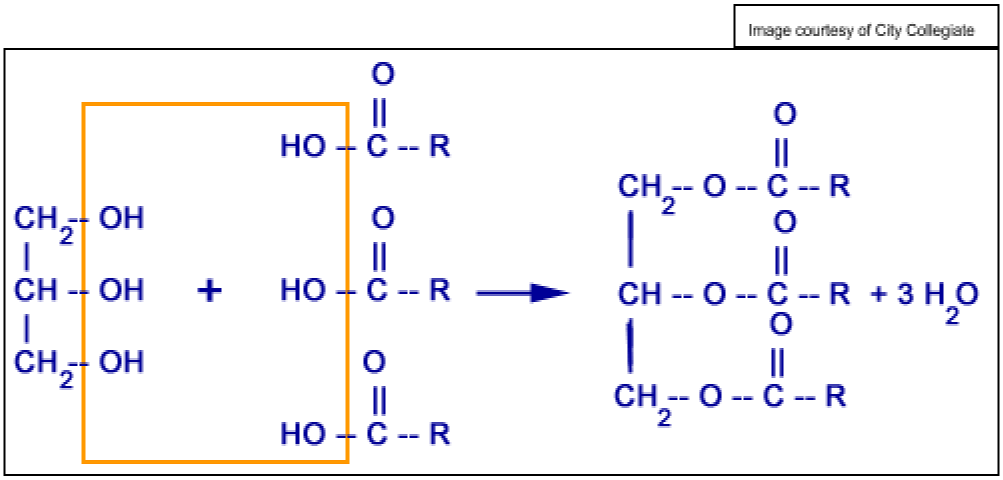
Organic Functional Groups and Reaction Mechanisms

Triglyceride Esters

Vegetable oils and fats are esters of naturally occuring **glycerol** (propane-1,2,3-triol). This alcohol undergoes esterification to form **triglyceride esters**. The chain length of the carboxylic acids range from C4 to C2. These acid molecules can also be saturated or unsaturated. Oils which are liquid at room temperature contain more carbon-carbon double bonds than fats which are solid at room temperature.

Oil has a lower melting point due to it being more **unsaturated**. The presence of carbon-carbon double bonds in the oil molecules changes the acids chains and the molecule's shape. As a result the molecules cannot pack closely together. This reduces the **Van der Waals/london forces** between the molecules, thus reducing the melting point.

Example:



Types of reactions

Reactions can be classified according to what happens to the reactants during the reaction and what the end products are. The main types of reaction are:

- **Addition** - the reactants combine to form a **single product.**
- **Substitution** - one functional group is **replaced** by a **different functional group**.
- **Oxidation** - a species **loses** at least one electron, and is oxidised.
- **Reduction** - a species **gains** at least one electron, and is reduced.
- **Hydrolysis** - A reaction in which a molecule is broken down by its reaction with water.
- **Condensation** - A reaction where two smaller molecules react to form a larger one, also producing a small molecule like water.
- **Elimination** - a small molecule is **removed** from a larger molecule.

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

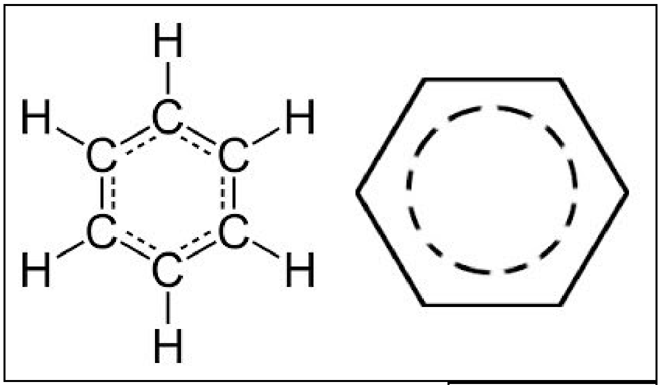


Image courtesy of Quora

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

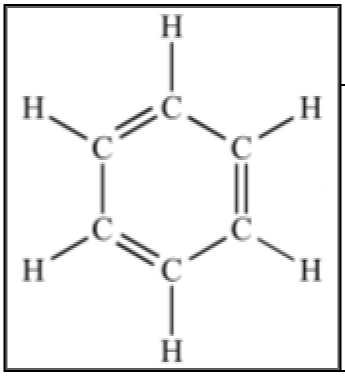


Image courtesy of www.chem.ucla.edu

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:

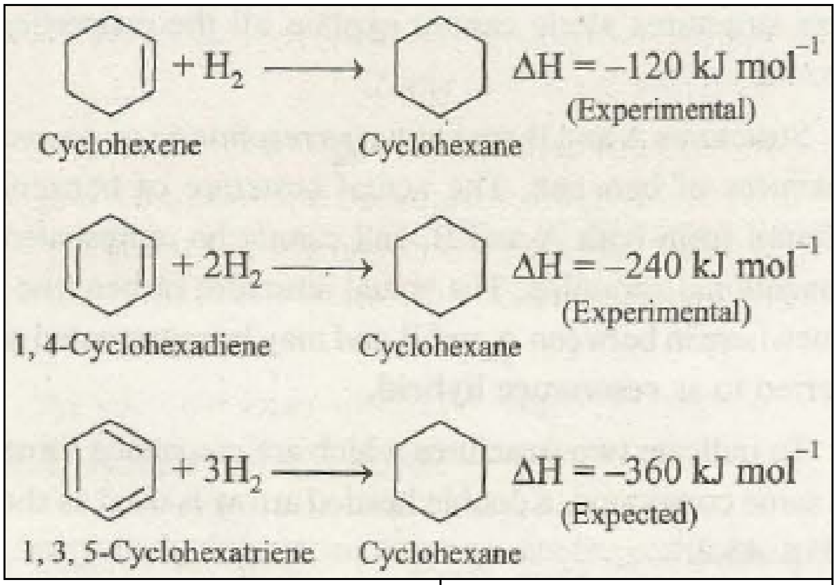


Image courtesy of chemistry-assignment.com

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.

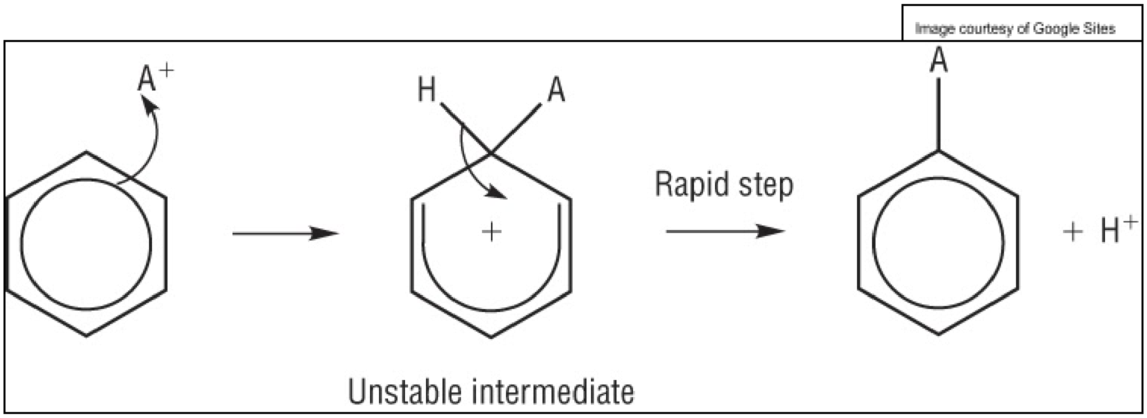
Reactions of Benzene

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



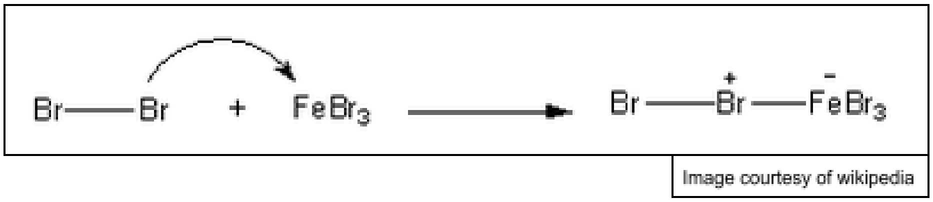
The electrophile is shown as A^+***.***

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.



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

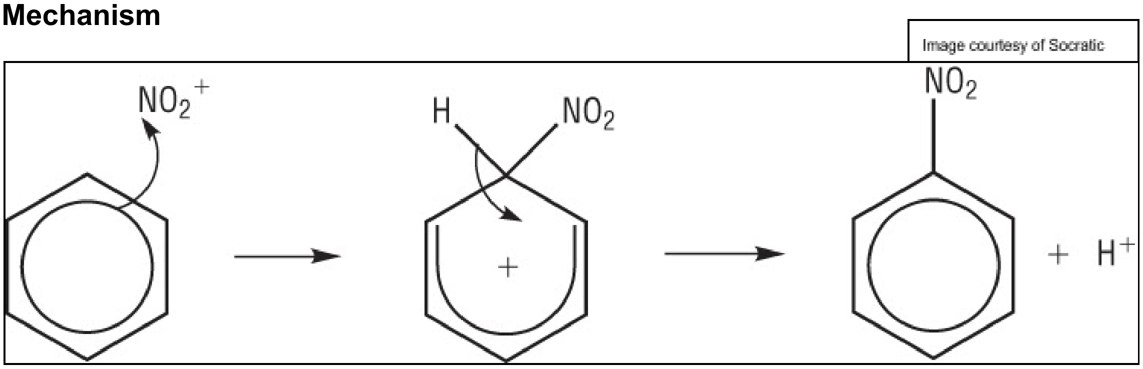


Image courtesy of Socratic

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**.

Sulfonation

When **sulfur trioxide** and **fuming sulfuric acid** are added to benzene, **benzenesulfonic acid** is produced via an electrophilic substitution mechanism.

Example:

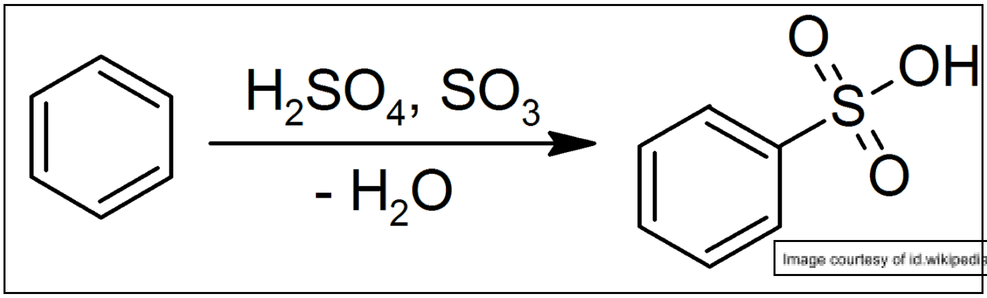


Image courtesy of id.wikipedia.org

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**.

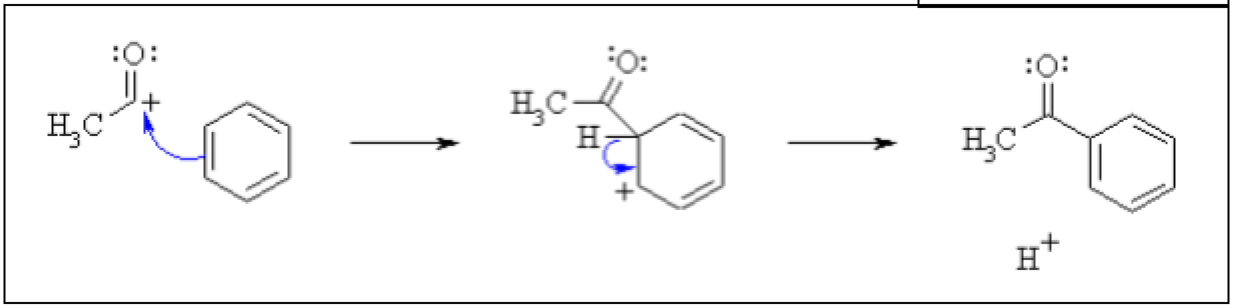
Example: Formation of the reactive intermediate

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

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.

Friedel-Crafts Alkylation

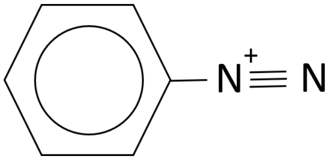
Alkylation of benzene involves the **substitution of an alkyl group**. The reaction occurs in the same way as the acylation reaction takes place above. It requires a **halogenoalkane** as a reactant as they contain a **polar bond** between the carbon and halogen.

Stage 1: $CH_3Cl + AlCl_3 \rightarrow AlCl_4^- + CH_3^+$

Stage 2: $CH_3^+ + C_6H_6 \rightarrow C_6H_5CH_3 + H^+$

Stage 3: $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

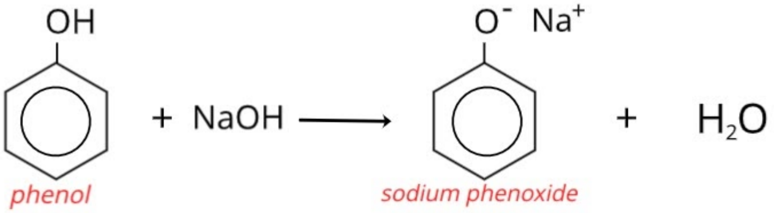
Diazonium Salts



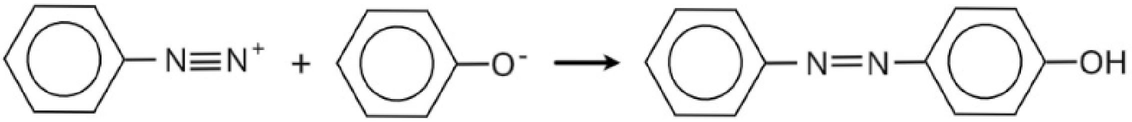
Diazonium salts are produced by standing a solution of phenylamine in hydrochloric acid (phenylammonium chloride solution) in an ice bath. Cold nitrate solution is added dropwise to the mixture, keeping the temperature low at all times. This produces a solution of **benzenediazonium chloride.**

Diazonium salts contain the diazonium ion, **R-N$_2^+$** (where R is any organic group). In the case of the following example, we will be looking at the diazonium ion when it is attached to a **benzene ring**.

Before a diazonium salt is reacted with phenol, phenol is dissolved in **sodium hydroxide** to give the **phenoxide ion**:



Cold **benzenediazonium chloride** is then added to the **sodium phenoxide** solution. The diazonium and phenoxide ions react together to form an **azo compound**. An azo compound contains two benzene rings that are joined together with a nitrogen bridge. The product can be identified as a **yellow solution** or **precipitate**.



These azo compounds are used in industry as **dyes**.

Reactions of Aldehydes

When heated under **reflux** conditions, aldehydes will be **oxidised** to produce **carboxylic acids**. The reagents used are $K_2Cr_2O_7$ and H_2SO_4 (acidified potassium dichromate). The oxidising agent is the dichromate ion, $Cr_2O_7^{2-}$.

Example:

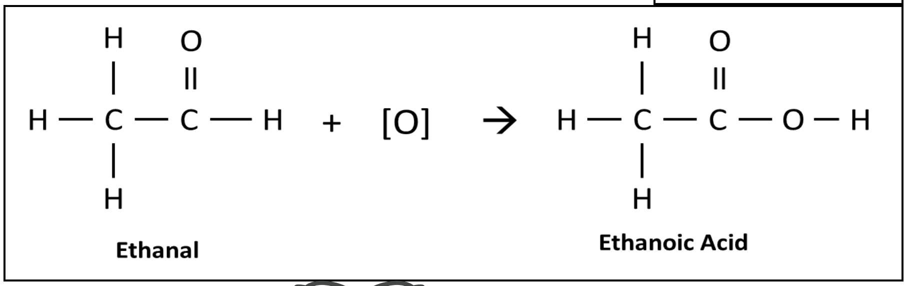


Image courtesy of anhourofchemaday

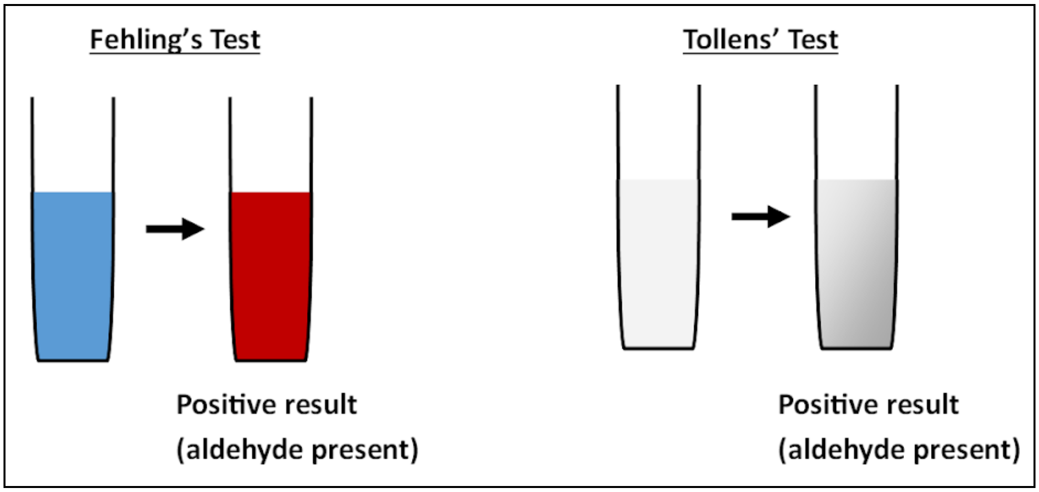
Test for Aldehydes and Ketones

Aldehydes are tested for using **Tollen's reagent** or **Fehling's solution** since they produce a positive result in both tests if present. Ketones will not give a positive result with either of these reagents. In these tests, the Fehling's solution/Tollen's reagent acts as an **oxidising agent**.

A few drops of **Fehling's solution** are added and the test tube is gently warmed. If an aldehyde is present a **red precipitate** will form. If a ketone is present the solution will remain **blue**.

Aldehydes can be tested in the same way using **Tollen's reagent.** If an aldehyde is present a layer of **silver** will form on the walls of the test tube. If a ketone is present the solution will remain colourless.

Example:



Hydroxynitriles

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/cyanohydrin**.

Mechanism:

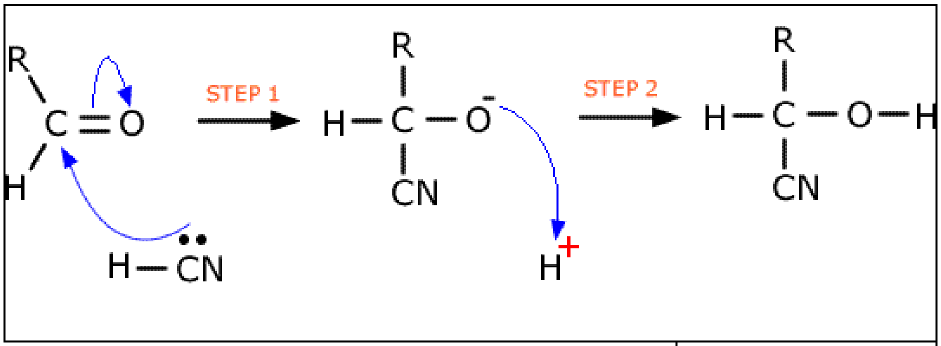


Image courtesy of Get Revising

KCN (potassium cyanide) is often used as the reagent to provide the nucleophile instead of **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 that the product exists as a mixture of optical isomers. The :CN- nucleophile can attack from either above or below the planar double bond, causing different **enantiomers** to be produced.

Polyfunctional Molecules

An organic compound which contains two or more functional groups is called a **polyfunctional compound**. When naming a polyfunctional molecule the following **IUPAC** rules are used:

1) One of the functional groups is the **principal functional group**, while the other groups are substituents which are identified by a prefix.
2) The principal chain will contain the maximum number of the functional groups as possible, and must contain the principal functional group.
3) When numbering the principal chain the principal functional group must be the lowest number possible.
4) The prefix for the secondary functional groups must be in alphabetical order.

Organic Synthesis

Synthesis pathways are needed to convert starting materials into a **target product**. This can sometimes be achieved through single-step reactions, but other times **multistep pathways** that, for example, oxidize functional groups, lengthen the carbon chain and saturate double bonds, are required.

When designing a synthetic pathway a chemist must consider several factors:

- Product yield (related to Le Chatelier's principle)
- Reaction set up, including:
  - Catalysts
  - Reagents
  - Conditions - temperature, pressure, concentrations
- The process involved - batch or continuous
- Hazards
- Cost
- Formation of isomers - for example, many drug targets are enzymes that are stereospecific and react with one enantiomer only. The synthetic pathway designed for these drugs should, ideally, only produce this enantiomer and not a racemic mixture.

Energy and Matter

Colour in Organic Molecules

Colour in organic molecules is often associated with carbon-carbon double bonds or **unsaturation**. This is due to the electrons in π bonds being able to be promoted to higher energy orbitals when **electromagnetic radiation** of a specific energy is absorbed. **Conjugation** (alternating single and double bonds) also plays a major part in this as it lowers the energy required to promote an electron. This means the energy required to promote an electron now comes from the UV to visible region of the electromagnetic spectrum. When a specific wavelength is absorbed by a molecule, then the colour we see are the wavelengths being **reflected** from the molecule- the **complementary colour.**

Modern Analytical Techniques

Gas-Liquid Chromatography (GC)

In gas-liquid chromatography, a **thin coiled column** is packed with a **high boiling point liquid adsorbed onto a solid** that acts as the stationary phase. Instead of a solvent, a **high pressure gas** is passed through this tube (an inert carrier gas like helium) and acts as the **mobile phase**. This method is used to separate mixtures of **volatile liquids** which are fed into the gas chromatography machine as vapours. Gas-liquid chromatography is also very sensitive and can detect very small traces of a substance. The analysis machine **records a retention time** for each component in the mixture, allowing them to be identified, as all substances have a unique retention time. A **mass spectrum** can also be taken to further help to identify emerging compounds.

Example: