WJEC Chemistry A-Level

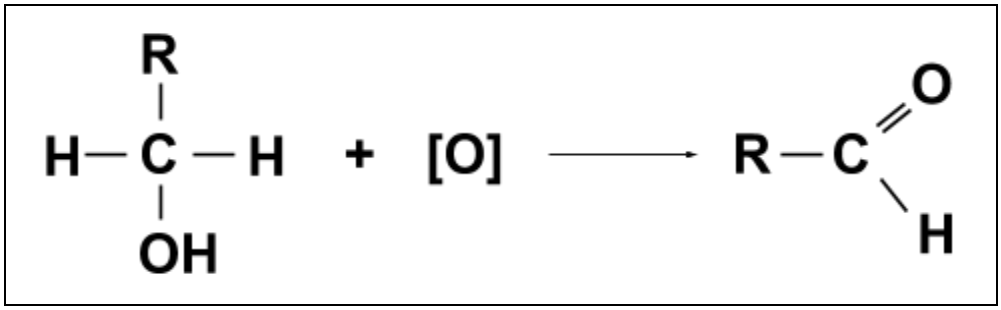
4.4: Aldehydes and Ketones

Detailed Notes

Welsh Specification

Aldehydes

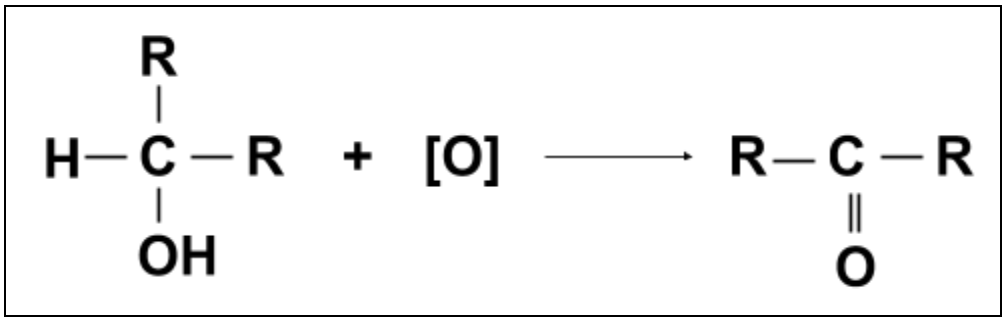
These organic compounds are recognised by the functional group **-CHO** containing a **carbonyl group (C=O)**. They are produced from the initial **oxidation and distillation of 1° alcohols**.
Example:



Aldehydes are tested for using Tollen's reagent or Fehling's solution as they produce a positive result in both tests if present. In Tollen's test, a silver mirror forms and in Fehling's test, the solution will turn brick red if an aldehyde is present.

Ketones

These organic compounds are recognised by the functional group -C=O, a carbonyl group. They are produced from the oxidation of 2^{o} alcohols with acidified potassium dichromate.
Example:

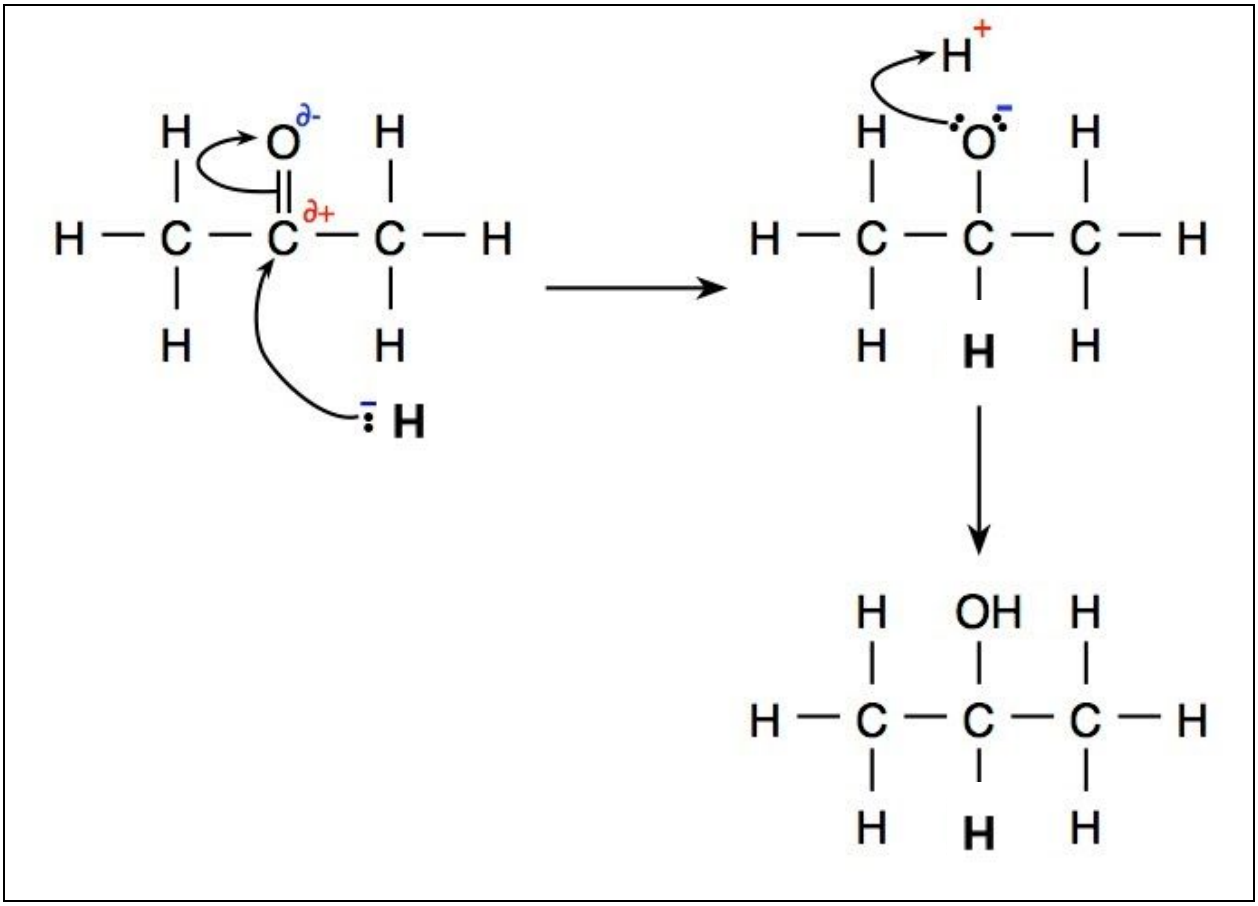


There is no further oxidation of ketones and they produce no visible change with both Tollen's reagent and Fehling's solution.

Reduction Reactions

All of the oxidation reactions involved in the production of aldehydes and ketones can be reversed in reduction reactions. For this, a reducing agent of $NaBH_4$ is used and the mechanism is an example of nucleophilic addition.

Mechanism



The reducing agent $NaBH_4$ provides the $H:^-$ nucleophile. However, a H^+ ion is also required so the reaction takes place under aqueous conditions so the water molecules can provide this ion.

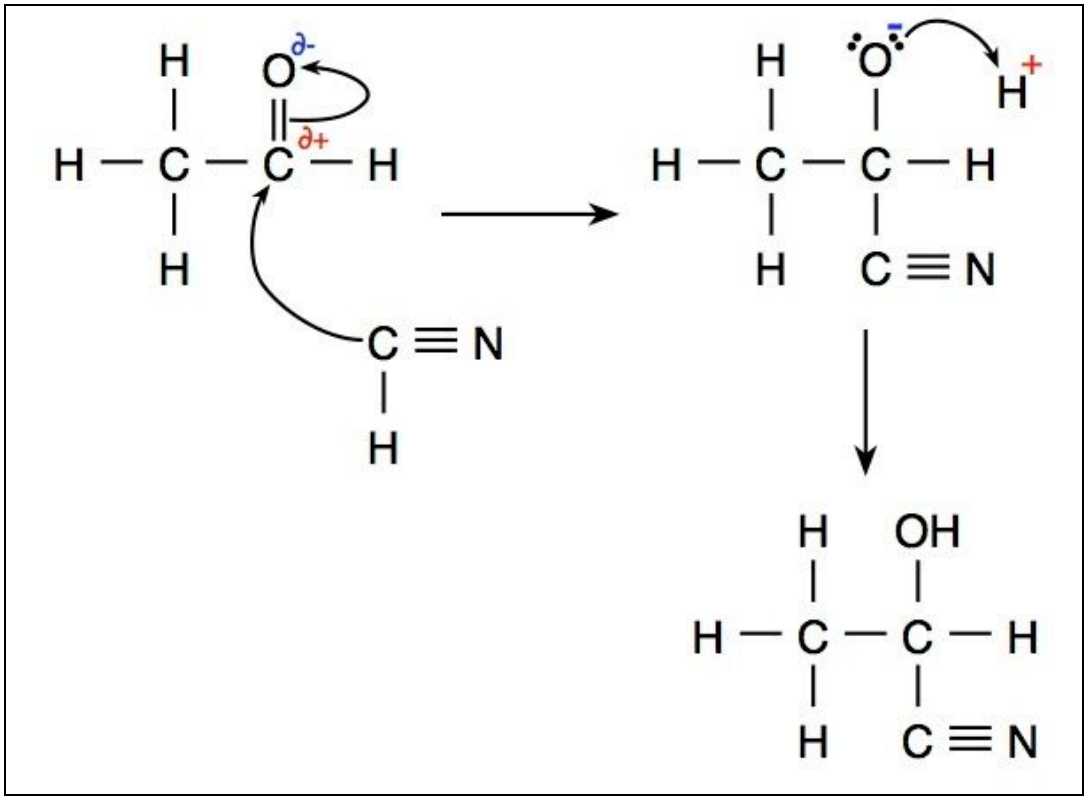
The mechanism is the same for the reduction of aldehydes to 1° alcohols.

Hydroxynitriles

Nucleophilic addition reactions are characteristic of aldehydes and ketones, especially those with the $:CN^-$ nucleophile. This is a form of organic synthesis as it causes an extension of the carbon chain by one carbon atom. The product of the reaction is a hydroxy-nitrile.

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 as a gas and reacts to produce dangerous byproducts.

Mechanism



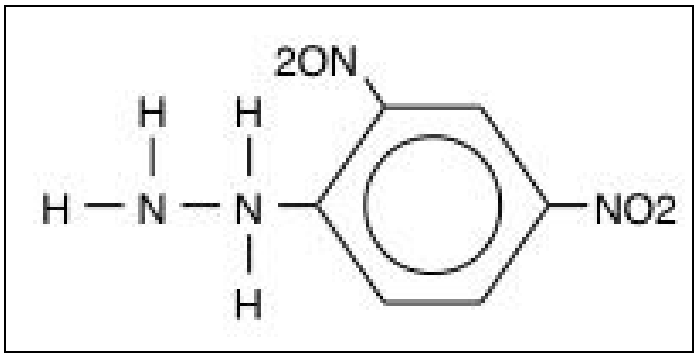
Hydroxy-nitriles commonly contain a chiral carbon centre meaning optical isomers of the product exist. The :CN- nucleophile can attack from either above or below the double bond, producing the two different enantiomers.

Tests for Aldehydes and Ketones

2-4-DNP

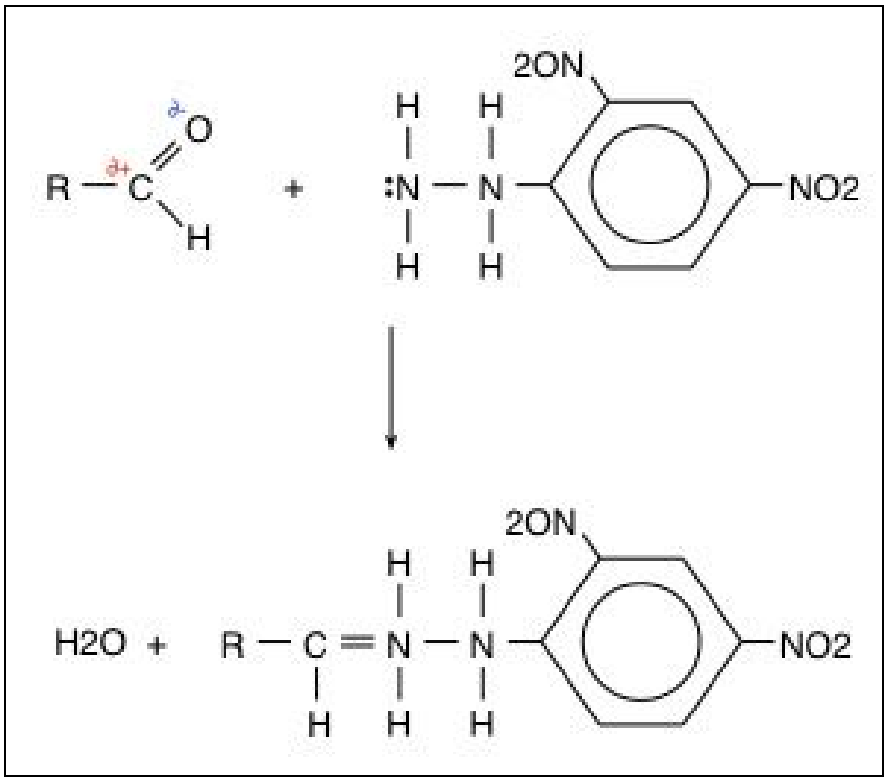
This molecule consists of nitrogen, hydrogen and a benzene ring with substituted nitro groups. It is often abbreviated to 2-4-DNP.

Example:



As a molecule, it can react with aldehydes and ketones via an addition-elimination reaction to produce 2-4-dinitrophenylhydrazone compounds. This can also be considered as a condensation reaction as the two molecules involved, combine and expel only water as a byproduct.

Mechanism



This reaction and therefore 2-4-DNP can be used as a test for aldehydes and ketones. If a carbonyl -C=O group is present, an orange-yellow precipitate will form. Further tests can then be carried out to find out the specific carbonyl molecule present including accurate measurement of melting point.

Iodoform Test

Iodine and sodium hydroxide solution can be combined as the reagents for this chemical test. It allows the presence of a CH_3CO group to be identified.

In the test, a small amount of iodine solution is added followed by just enough sodium hydroxide to remove the colour of the iodine. If this group is present, a pale yellow precipitate of triiodomethane (iodoform) is produced.