This page gives you the facts and simple, uncluttered mechanisms for the nucleophilic addition reactions between carbonyl compounds (specifically aldehydes and ketones) and hydrogen cyanide, HCN.

The reaction of aldehydes and ketones with hydrogen cyanide

Hydrogen cyanide adds across the carbon-oxygen double bond in aldehydes and ketones to produce compounds known as hydroxynitriles. For example, with ethanal (an aldehyde) you get 2-hydroxypropanenitrile:

$$\text{CH}_3\text{C}=\text{O} + \text{HCN} \rightarrow \text{CH}_3\text{C}(-\text{CN})\text{H}$$

With propanone (a ketone) you get 2-hydroxy-2-methylpropanenitrile:

$$\text{CH}_3\text{C}=\text{O} + \text{HCN} \rightarrow \text{CH}_3\text{C}(-\text{CN})\text{H}_2$$

The reaction isn't normally done using hydrogen cyanide itself, because this is an extremely poisonous gas. Instead, the aldehyde or ketone is mixed with a solution of sodium or potassium cyanide in water to which a little sulphuric acid has been added. The pH of the solution is adjusted to about 4 - 5, because this gives the fastest reaction. The solution will contain hydrogen cyanide (from the reaction between the sodium or potassium cyanide and the sulphuric acid), but still contains some free cyanide ions. This is important for the mechanism.

The mechanisms

These are examples of nucleophilic addition. The carbon-oxygen double bond is highly polar, and the slightly positive carbon atom is attacked by the cyanide ion acting as a nucleophile.

The mechanism for the addition of HCN to propanone

In the first stage, there is a nucleophilic attack by the cyanide ion on the slightly positive carbon atom.
The negative ion formed then picks up a hydrogen ion from somewhere - for example, from a hydrogen cyanide molecule.

The hydrogen ion could also come from the water or the $H_3O^+$ ions present in the slightly acidic solution. You don't need to remember all of these. One equation is perfectly adequate.

**The mechanism for the addition of HCN to ethanal**

As before, the reaction starts with a nucleophilic attack by the cyanide ion on the slightly positive carbon atom.

It is completed by the addition of a hydrogen ion from, for example, a hydrogen cyanide molecule.

**Optical isomerism in 2-hydroxypropanenitrile**

When 2-hydroxypropanenitrile is made in this last mechanism, it occurs as a racemic mixture - a 50/50 mixture of two optical isomers. It is possible that you might be expected to explain how this arises. Optical isomerism occurs in compounds which have four different groups attached to a single carbon atom. In this case, the product molecule contains a CH$_3$, a CN, an H and an OH all attached to the central carbon atom.
The reason for the formation of equal amounts of two isomers lies in the way the ethanal gets attacked. Ethanal is a planar molecule, and attack by a cyanide ion will either be from above the plane of the molecule, or from below. There is an equal chance of either happening.

Attack can be from here...

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

...or from here.

Attack from one side will lead to one of the two isomers, and attack from the other side will lead to the other.

All aldehydes will form a racemic mixture in this way. Unsymmetrical ketones will as well. (A ketone can be unsymmetrical in the sense that there is a different alkyl group either side of the carbonyl group.) What matters is that the product molecule must have four different groups attached to the carbon which was originally part of the carbon-oxygen double bond.

Contributors

- Jim Clark (Chemguide.co.uk)