Objectives

After completing this section, you should be able to

1. write an equation to describe the formation of a cyanohydrin from an aldehyde or ketone.
2. identify the cyanohydrin formed from the reaction of a given aldehyde or ketone with hydrogen cyanide.
3. identify the aldehyde or ketone, the reagents, or both, needed to prepare a given cyanohydrin.
4. write the detailed mechanism for the addition of hydrogen cyanide to an aldehyde or ketone.

Key Terms

Make certain that you can define, and use in context, the key term below.

• cyanohydrin

Study Notes

For successful cyanohydrin formation it is important to have free cyanide ions available to react with the ketone or aldehyde. This can be achieved by using a salt (e.g. KCN or NaCN) or a silylated (e.g. Me₃SiCN) form of cyanide under acidic conditions or by using HCN with some base added to produce the needed CN⁻ nucleophile.

Cyanohydrins have the structural formula of R₂C(OH)CN. The “R” on the formula represents an alkyl, aryl, or hydrogen. To form a cyanohydrin, a hydrogen cyanide adds reversibly to the carbonyl group of an organic compound thus forming a hydroxyalkanenitrile adducts (commonly known and called as cyanohydrins).

\[
\begin{align*}
\text{N} & \\
\text{C} & \\
\text{C} & \\
\text{R} & \\
\text{R'} & \\
\text{OH} & 
\end{align*}
\]

*Figure 19.6.1: General structure of a cyanohydrin*

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

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.

**Mechanism of Cyanohydrin Formation**

Acid-catalyzed hydrolysis of silylated cyanohydrins has recently been shown to give cyanohydrins instead of ketones; thus an efficient synthesis of cyanohydrins has been found which works with even highly hindered ketones.

**Acetone Cyanohydrins**

Acetone cyanohydrins (ACH) have the structural formula of \((\text{CH}_3)_2\text{C(OH)CN}\). It is an organic compound serves in the production of methyl methacrylate (also known as acrylic).
Figure 19.6.2: Acetone cyanohydrins

It is classified as an extremely hazardous substance, since it rapidly decomposes when it's in contact with water. In ACH, sulfuric acid is treated to give the sulfate ester of the methacrylamid. Preparations of other cyanohydrins are also used from ACH: for HACN to Michael acceptors and for the formylation of arenas. The treatment with lithium hydride affords anhydrous lithium cyanide.

![Figure 19.6.3: Reduction of Acetone cyanohydrins](image)

Other Cyanohydrins

Other cyanohydrins, excluding acetone cyanohydrins, are: mandelonitrile and glycolonitrile.

![Figure 19.6.4: Structures of Madelonitrile (left) and glycolonitrile (right)](image)

Mandelonitrile have a structural formula of $\text{C}_6\text{H}_5\text{CH(OH)CN}$ and occur in pits of some fruits. Glycolonitrile is an organic compound with the structural formula of $\text{HOCH}_2\text{CN}$, which is the simplest cyanohydrin that is derived by formaldehydes.

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